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(54) Title: DUAL CURE COATING COMPOSITIONS HAVING IMPROVED SCRATCH RESISTANCE, COATED SUBSTRATES AND METHODS RELATED THERETO

(57) Abstract: Coating compositions formed from components including radiation and thermally curable material(s); curing agent(s) and a plurality of particles are provided, wherein each component is different. Also provided are multi-component composite coatings which include a cured basecoat deposited from a pigmented coating composition and a cured topcoat deposited from a topcoating composition. The multi-component composite coatings of the invention provide highly scratch resistant color-plus-clearcoatings.

**DUAL CURE COATING COMPOSITIONS HAVING
IMPROVED SCRATCH RESISTANCE, COATED
SUBSTRATES AND METHODS RELATED THERETO**

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FIELD OF THE INVENTION

Certain embodiments of the present invention generally are directed to dual cure coating compositions formed from radiation curable materials, thermally 10 durable materials, curing agents, and a plurality of particles, wherein each component is different. Other embodiments of the present invention generally are directed to dual cure coating compositions formed from materials having at least one radiation curable group and at least one thermally curable group, curing agents; and a plurality of particles, wherein each component is different. Other 15 embodiments of the present invention are directed to substrates coated with the aforementioned cured compositions. Further embodiments of the present invention are directed to methods for improving scratch resistance of a substrate. It will be apparent to one of ordinary skill in the art that specific embodiments of the present invention may be directed to some or all of these aspects of the 20 present invention as well as other desirable aspects.

BACKGROUND OF THE INVENTION

Over the past decade, there has been a concerted effort to reduce atmospheric pollution caused by volatile solvents which are emitted during the 25 painting process. However, it is often difficult to achieve high quality, smooth coating finishes, such as are required in the industrial and automotive industry, without using organic solvents, which contribute greatly to flow and leveling of a coating. In addition to achieving near-flawless appearance, such coatings must be durable and abrasion resistant, yet economical and easy to apply.

30 The use of conventional thermally curable thermosetting resins for coating compositions can be undesirable because of the necessity for thinning the resins with solvents to provide easy application to substrates. The use of solvents is undesirable for cost and environmental reasons because the solvents must be removed from the coating composition during cure.

To alleviate the above problems, radiation sensitive materials have been developed which cure by ionizing or actinic radiation, which lessen or eliminate the need for solvent. However, the flexibility of radiation cure coatings can be less than desired and the properties of such coating compositions are not easily modified for different applications.

- U.S. Patent No. 4,025,407 discloses thinning conventional thermosetting resins with radiation or actinic light sensitive materials and subjecting the coatings to ionizing or actinic radiation and then to conventional curing mechanisms for thermosetting resins. In Example 1, a thermosetting resin was formed by mixing,
- 10 *inter alia*, a radiation sensitive monomer with a radiation insensitive aliphatic diisocyanate, TiO₂ and black tint, subjecting the coating to electron beam irradiation and then moisture curing the coating by heating at 140°F for 24 hours.

U.S. Patent No. 5,571,297 discloses a binder coat which comprises a mixture of abrasive grit and a compound having at least one function that is

15 radiation curable and at least one function that is thermally curable

- Color-plus-clearcoating systems involving the application of a colored or pigmented basecoat to a substrate followed by application of a transparent or clearcoat over the basecoat have become increasingly popular as original finishes for a number of consumer products including, for example automotive vehicles.
- 20 The color-plus-clearcoating systems have outstanding appearance properties such as gloss and distinctness of image, due in large part to the clearcoat. Such color-plus-clearcoating systems have become popular for use with automotive vehicles, aerospace applications, floor coverings such as ceramic tiles and wood flooring, packaging coatings and the like.
- 25 Topcoat film-forming compositions, particularly those used to form the transparent clearcoat in color-plus-clearcoating systems for automotive and industrial applications, are subject to defects that occur during the assembly process as well as damage from numerous environmental elements. Such defects during the assembly process include paint defects in the application or
- 30 curing of the basecoat or the clearcoat. Damaging environmental elements include acidic precipitation, exposure to ultraviolet radiation from sunlight, high

relative humidity and high temperatures, defects due to contact with objects causing scratching of the coated surface, and defects due to impact with small, hard objects resulting in chipping of the coating surface.

- Typically, a harder more highly crosslinked film may exhibit improved
- 5 scratch resistance, but it is less flexible and much more susceptible to chipping and/or thermal cracking due to embrittlement of the film resulting from a high crosslink density. A softer, less crosslinked film, while not prone to chipping or thermal cracking, is susceptible to scratching, waterspotting, and acid etch due to a low crosslink density of the cured film.
- 10 Further, elastomeric automotive parts and accessories, for example elastomeric bumpers and hoods, are typically coated "off site" and shipped to automobile assembly plants. The coating compositions applied to such elastomeric substrates are typically formulated to be very flexible so the coating can bend or flex with the substrate without cracking. To achieve the requisite
- 15 flexibility, coating compositions for use on elastomeric substrates often are formulated to produce coatings with lower crosslink densities or to include flexibilizing adjuvants which act to lower the overall film glass transition temperature (Tg). While acceptable flexibility properties can be achieved with these formulating techniques, they also can result in softer films that are
- 20 susceptible to scratching. Consequently, great expense and care must be taken to package the coated parts to prevent scratching of the coated surfaces during shipping to automobile assembly plants.

- U.S. Patent No. 4,822,828 teaches the use of a vinyl functional silane in an aqueous, radiation curable, coating composition which comprises: (a) from 50 to
- 25 85 percent, based on the total weight of the dispersion, of a vinyl functional silane, (b) from 15 to 50 percent, based on the total weight of the dispersion of a multifunctional acrylate, and (c) optionally, from 1 to 3 weight percent of a photoinitiator. The vinyl-functional silane is the partial condensate of silica and a silane, such that at least sixty percent of the silane is a vinyl-functional silane
- 30 conforming to the formula $(R)_aSi(R')_b(R'')_c$ wherein R is allyl or vinyl functional alkyl; R' is hydrolyzable alkoxy or methoxy; R'' is non-hydrolyzable, saturated

alkyl, phenyl, or siloxy, such that $a+b+c=4$; and $a \geq 1$; $b \geq 1$; $c \geq 0$. The patent discloses that these coating compositions may be applied to plastic materials and cured by exposure to ultraviolet or electron beam irradiation to form a substantially clear, abrasion resistant layer.

- 5 Despite recent improvements in color-plus-clearcoating systems, there remains a need in the automotive coatings art for topcoats having good scratch resistance without embrittlement of the film. Moreover, it would be advantageous to provide topcoats for elastomeric substrates utilized in the industrial and automotive industries which are both flexible and resistant to scratching.

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SUMMARY OF THE INVENTION

- In one embodiment, the present invention is directed to a coating composition formed from components comprising: (a) at least one first material comprising at least one radiation curable reactive functional group; (b) at least one second material comprising at least one thermally curable reactive functional group; (c) at least one curing agent reactive with the at least one thermally curable reactive functional group, the at least one curing agent being selected from aminoplast resins, polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing; and (d) a plurality of particles selected from inorganic particles, composite particles, and mixtures of the foregoing, wherein each component is different.

- In another embodiment, the present invention is directed to a coating composition formed from components comprising: (a) at least one material comprising at least one ultraviolet radiation curable reactive functional group and at least one thermally curable reactive functional group; (b) at least one curing agent reactive with the at least one thermally curable reactive functional group, the at least one curing agent being selected from polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing; and (c) a plurality of particles, wherein each component is different.

Additionally, a coated substrate is disclosed to be within the scope of the

- present invention which comprises a substrate and a cured composition coated over at least a portion of the substrate, the cured composition being any of the foregoing cured compositions according to the present invention. The present invention also provides a method of coating a substrate which comprises forming
- 5 over at least a portion of the substrate a cured composition, the cured composition being any of the foregoing cured compositions according to the present invention. Coated automotive substrates also are disclosed to be within the present invention which comprise an automotive substrate which is coated, at least in part, by any of the foregoing cured compositions according to the present invention.
- 10 The present invention also provides methods of making coated automotive substrates comprising obtaining an automotive substrate and forming over at least a portion of the automotive substrate any of the foregoing cured compositions according to the present invention.

Also provided are multi-component composite coating compositions which

15 comprise a basecoat deposited from a pigmented coating composition, and any one of the foregoing cured compositions according to the present invention formed as a topcoat over the basecoat. The present invention also provides methods for making multi-component composite coating compositions comprising:

(a) applying a pigmented composition to a substrate to form a basecoat; and (b)

20 applying any one of the foregoing coating compositions as a topcoating composition over at least a portion of the basecoat, and (c) curing the topcoating composition to form any of the foregoing cured compositions according to the present invention.

Methods of improving the scratch resistance of a polymeric substrate or

25 polymeric coating which comprise forming on the polymeric substrate or polymeric coating any of the foregoing cured compositions according to the present invention also are provided in another embodiment of the present invention. The present invention also provides methods for retaining the gloss of a polymeric substrate or polymeric coating over time which comprises forming over at least a

30 portion of the polymeric substrate or polymeric coating any of the foregoing cured compositions according to the present invention. Also provided are methods for

revitalizing the gloss of a polymeric substrate or polymeric coating comprising forming over at least a portion of the polymeric substrate or polymeric coating any of the foregoing cured compositions according to the present invention.

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment, the present invention is directed to coating compositions formed from components comprising at least one first material comprising at least one radiation curable reactive functional group; at least one second material comprising at least one thermally curable reactive functional group; at least one curing agent reactive with the at least one thermally curable reactive functional group; and a plurality of particles, wherein each component is different. As used herein, "material" can be a compound, monomer, oligomer or polymer. In an alternative embodiment, in lieu of or in addition to the first and second materials, the film-forming material can comprise at least one functional

group which is curable by thermal energy and at least one functional group which is curable by ionizing or actinic radiation.

As used herein, the phrase "each component is different" refers to components which do not have the same chemical structure as other components
5 in the composition.

As used herein, the term "cure" as used in connection with a composition, e.g., "a cured composition," shall mean that at least a portion of the crosslinkable components which form the composition are at least partially crosslinked. In certain embodiments of the present invention, the crosslink density of the
10 crosslinkable components, i.e., the degree of crosslinking, ranges from 5% to 100% of complete crosslinking. In other embodiments, the crosslink density ranges from 35% to 85% of full crosslinking. In other embodiments, the crosslink density ranges from 50% to 85% of full crosslinking. The crosslinking density may range between any combination of these values inclusive of the recited values.
15 One skilled in the art will understand that the presence and degree of crosslinking, i.e., the crosslink density, can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a TA Instruments DMA 2980 DMTA analyzer conducted under nitrogen. This method determines the glass transition temperature and crosslink density of free films of coatings or polymers.
20 These physical properties of a cured material are related to the structure of the crosslinked network.

As discussed above, the compositions according to the present invention are formed from components comprising at least one first material comprising at least one radiation curable reactive functional group which is curable by ionizing
25 radiation and/or actinic radiation.

As used herein, "ionizing radiation" means high energy radiation and/or the secondary energies resulting from conversion of this electron or other particle energy to neutron or gamma radiation, said energies being at least 30,000 electron volts and can be 50,000 to 300,000 electron volts. While various types of
30 ionizing irradiation are suitable for this purpose, such as X-ray, gamma and beta rays, the radiation produced by accelerated high energy electrons or electron

beam devices also can be used. The amount of ionizing radiation in rads for curing compositions according to the present invention can vary based upon such factors as the components of the coating formulation, the thickness of the coating upon the substrate, the temperature of the coating composition and the like.

- 5 Generally, a 1 mil (25 micrometer) thick wet film of a coating composition according to the present invention can be cured in the presence of oxygen through its thickness to a tack-free state upon exposure to from 0.5 to 5 megarads of ionizing radiation.

"Actinic radiation" is light with wavelengths of electromagnetic radiation ranging from the ultraviolet ("UV") light range, through the visible light range, and into the infrared range. Actinic radiation which can be used to cure coating compositions of the present invention generally has wavelengths of electromagnetic radiation ranging from 150 to 2,000 nanometers (nm), from 180 to 1,000 nm, or from 200 to 500 nm. In one embodiment, ultraviolet radiation having a wavelength ranging from 10 to 390 nm can be used. Examples of suitable ultraviolet light sources include mercury arcs, carbon arcs, low, medium or high pressure mercury lamps, swirl-flow plasma arcs and ultraviolet light emitting diodes. Suitable ultraviolet light-emitting lamps are medium pressure mercury vapor lamps having outputs ranging from 200 to 600 watts per inch (79 to 237 watts per centimeter) across the length of the lamp tube. Generally, a 1 mil (25 micrometer) thick wet film of a coating composition according to the present invention can be cured through its thickness to a tack-free state upon exposure to actinic radiation by passing the film at a rate of 20 to 1000 feet per minute (6 to 300 meters per minute) under four medium pressure mercury vapor lamps of exposure at 200 to 1000 millijoules per square centimeter of the wet film.

The at least one radiation curable reactive functional group can be selected from vinyl groups, vinyl ether groups, epoxy groups, maleimide groups, fumarate groups and combinations of the foregoing. Suitable first materials having vinyl functionality include those having unsaturated ester groups and vinyl ether groups as discussed below. A non-limiting example of suitable epoxy groups includes cycloaliphatic epoxy groups.

- Suitable first materials comprising unsaturated ester groups include materials comprising acrylate groups, methacrylate groups and/or ethacrylate groups. The unsaturated ester group can be an acrylate group. Useful materials comprising unsaturated ester groups include esters and amides of acrylic or
- 5 methacrylic acid or comonomers of such an ester with another copolymerizable monomer. Suitable esters include methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl(meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol (meth)acrylate, tetraethylene
- 10 glycol di(meth)acrylate, glycerol di(meth)acrylate, glycerol tri(meth)acrylate, 1,3-propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,2,4-butanetriol tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, 1,4-benzenediol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, 1,5-pentanediol
- 15 di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, (meth)acrylates derived from aromatic glycidyl ethers such as bisphenol A diglycidyl ethers and aliphatic diglycidyl ethers, acrylic or methacrylic amides such as
- 20 (meth)acrylamide, diacetone (meth)acrylamide, N-(betahydroxyethyl) (meth)acrylamide, N,N-bis(betahydroxyethyl) (meth)acrylamide, methylene bis(meth)acrylamide, 1,6-hexamethylene bis(meth)acrylamide, diethylenetriamine tris(meth)acrylamide, bis(gamma-(meth)acrylamidepropoxy) ethane, beta-(meth)acrylamide ethylacrylate and mixtures of the foregoing.
- 25 Other useful first materials comprising unsaturated ester groups include hydroxy functional unsaturated polycarboxylates and polycaprolactones. Suitable hydroxy functional unsaturated polycarboxylates can be formed from ethylenically unsaturated carboxylic acids and polyhydric alcohols. Useful ethylenically unsaturated carboxylic acids have an acid functionality of at least two and/or their
- 30 corresponding anhydrides. Non-limiting examples of ethylenically unsaturated carboxylic acids and anhydrides include maleic acid, maleic anhydride, fumaric

acid, itaconic acid and mixtures of the foregoing. The unsaturated carboxylic acids can be blended with saturated carboxylic acids, such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, suberic acid, 2,2-dimethylsuccinic acid, 2,2-dimethylglutaric acid, 3,3-dimethylglutaric acid, anhydrides of the foregoing, where they exist, and mixtures of any of the foregoing.

Useful polyhydric alcohols for preparing the hydroxy functional unsaturated polycarboxylate include diethylene glycol, ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,2-bis(hydroxyethyl)cyclohexane, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, neopentyl glycol, 2-methyl-1,3-propane diol and mixtures of the foregoing. Monofunctional alcohols, such as C₁-C₁₅ monoalcohols, can be blended with the polyhydric alcohols, as desired.

The number average molecular weight of the unsaturated ester material can range from 500 to 50,000 grams per mole, as measured using gel permeation chromatography using a polystyrene standard. The unsaturated ester material can be prepared by any method well known to those skilled in the art, such as by mixing the components and heating at temperatures ranging from 150°C to 250°C for 1 to 10 hours and removing water formed during the esterification reaction. Conventional esterification catalysts, such as paratoluenesulfonic acid, butylstannoic acid, dibutyltin oxide, stannous fluoride and stannous octoate can be used to increase the rate of reaction.

Vinyl ether functional materials suitable for use in the present invention include vinyl ethers prepared from di-, tri- or tetrafunctional polyols, acetylene and a basic catalyst under pressure in a manner well known to those skilled in the art. Also, vinyl terminated polyesters such as those disclosed in U.S. Patent No. 5,286,835 (incorporated herein by reference) can be used. Non-limiting examples of useful vinyl ether functional materials include tripropylene glycol divinyl ether,

diethylene glycol divinyl ether, 1,4-butanediol divinyl ether, tetraethylene glycol divinyl ether, triethylene glycol divinyl ether, trimethylolpropane trivinyl ether, polytetrahydrofuran divinyl ether, vinyl ether terminated polyesters and mixtures of the foregoing. Also useful are unsaturated ester materials having vinyl ether functionality and urethane vinyl ether materials, such as are disclosed in U.S. Patent No. 5,942,556 (incorporated herein by reference).

Other useful first materials comprising epoxy functional groups include epoxy functional monomers such as glycidyl methacrylate and polymers having at least two epoxide or oxirane groups per molecule. These materials often are referred to as di- or polyepoxides. Generally, the epoxide equivalent weight of the epoxy-functional polymer can range from 128 to 2800, as measured by titration with perchloric acid and quaternary ammonium bromide using methyl violet as an indicator.

Suitable epoxy-functional polymers can be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. The epoxy-functional polymers can have pendant or terminal hydroxyl groups, if desired. They can contain substituents such as halogen, hydroxyl, and ether groups. A useful class of these materials include polyepoxides obtained by reacting an epihalohydrin (such as epichlorohydrin or epibromohydrin) with a di- or polyhydric alcohol in the presence of an alkali. Suitable polyhydric alcohols include polyphenols such as resorcinol; catechol; hydroquinone; bis(4-hydroxyphenyl)-2,2-propane, i.e., bisphenol A; bis(4-hydroxyphenyl)-1,1-isobutane; 4,4-dihydroxybenzophenone; bis(4-hydroxyphenol)-1,1-ethane; bis(2-hydroxyphenyl)-methane and 1,5-hydroxynaphthalene.

Examples of useful polyepoxides include diglycidyl ethers of bisphenol A, such as EPON® 828 epoxy resin which is commercially available from Shell Chemical Company. Other useful polyepoxides include polyglycidyl ethers of polyhydric alcohols, polyglycidyl esters of polycarboxylic acids, polyepoxides that are derived from the epoxidation of an olefinically unsaturated alicyclic compound, polyepoxides containing oxyalkylene groups in the epoxy molecule, epoxy novolac resins, and polyepoxides that are partially defunctionalized by carboxylic acids,

alcohol, water, phenols, mercaptans or other active hydrogen-containing compounds to give hydroxyl-containing polymers.

The first material, when added to other components that form the coating composition; is present in the coating composition in an amount ranging from 1 to 5 99 weight percent based on total weight of the resin solids of the components which form the coating composition, from 25 to 95 weight percent or from 50 to 95 weight percent.

As used herein "based on total weight of the resin solids" of the composition means that the amount of the component added during the formation 10 of the composition is based upon the total weight of the solids (non-volatiles) of any film-forming component, any polysiloxane, any curing agent present during the formation of the coating composition, and any silyl-blocked material present, but not including the particles, any solvent, or any additive solids such as hindered 15 amine stabilizers, photoinitiators, pigments including extender pigments and fillers, catalysts, flow modifiers, and UV light absorbers.

In one embodiment, the present invention is directed to a coating composition in which the first material comprises at least one polysiloxane comprising reactive functional groups which can be curable by ionizing radiation or actinic radiation. In another embodiment, the polysiloxane can comprise at 20 least one functional group which is curable by thermal energy and at least one functional group which is curable by ionizing or actinic radiation.

In one embodiment of the present invention, the at least one polysiloxane has at least one radiation curable functional group selected from vinyl groups, epoxy groups, maleimide groups, fumarate groups and combinations of the 25 foregoing as are described above. The general structure of the polysiloxane will be discussed below in the discussion of the thermally curable second material. The at least one polysiloxane having at least one radiation curable functional group can be present in the components from which the coating composition is formed in an amount ranging from 0.5 to 95 weight percent on a basis of total 30 weight of the resin solids of the components which form the coating composition, from 25 to 95 weight percent or from 50 to 95 weight percent. The amount of the

first material may range between any combination of these values inclusive of the recited values.

The components from which the coating composition is formed can comprise, in addition to the first material, at least one other ethylenically

- 5 unsaturated monomer or oligomer as desired, including but not limited to vinyl monomers such as vinyl acetate, styrene, vinyl toluene, divinyl benzene, methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether and mixtures thereof. The at least one other ethylenically unsaturated monomer or oligomer can be present in the components from which the coating composition is formed in an amount ranging
- 10 from 1 to 99 weight percent based on total weight of the resin solids of the components which form the coating composition, can range from 25 to 95 weight percent or can range from 50 to 95 weight percent. The amount of the at least one other ethylenically unsaturated monomer or oligomer may range between any combination of these values inclusive of the recited values.
- 15 In another embodiment in which the coating is cured by actinic radiation or the combination of actinic radiation and thermal energy, the components from which the coating composition are formed further can comprise at least one photoinitiator or photosensitizer which provides free radicals or cations to initiate the polymerization process. Useful photoinitiators have an adsorption in the range
- 20 of 150 to 2,000 nm. Non-limiting examples of useful photoinitiators include benzoin, benzophenone, hydroxy benzophenone, anthraquinone, thioxanthone, substituted benzoins such as butyl isomers of benzoin ethers, α,α -diethoxyacetophenone, α,α -dimethoxy- α -phenylacetophenone, 2-hydroxy-2-methyl-1-phenyl propan-1-one, 2,4,6-trimethyl benzoyl diphenyl phosphine oxide
- 25 and mixtures of the foregoing. Non-limiting examples of suitable cationic photoinitiators include iodonium salts such as FC 509® available from 3M, and sulfonium salts such as UVI-6991 and UVI-6974 available from Union Carbide. The photoinitiator can be a 50:50 blend of 2-hydroxy-2-methyl-1-phenyl propan-1-one and 2,4,6-trimethyl benzoyl diphenyl phosphine oxide such as DAROCURE
- 30 4265, which is commercially available from Ciba-Geigy Corporation.

In one embodiment, the components from which the coating composition is

formed comprise at least one second material comprising at least one thermally curable reactive functional group. Useful thermally curable reactive functional groups include hydroxyl groups, vinyl groups, urethane groups, urea groups, amide groups, carbamate groups, isocyanate groups, blocked isocyanate groups,

5 epoxy groups, acid groups, amine groups, anhydride groups, and aziridine groups. In one embodiment, the at least one second material can have at least one reactive functional group selected from a hydroxyl group, a carbamate group, an epoxy group, an isocyanate group, and a carboxyl group. In another embodiment, the at least one second material can have at least one reactive

10 functional group selected from a hydroxyl group and a carbamate group.

The second material can be a film-forming polymer selected from hydroxyl functional polymers, polyesters, acrylic polymers, polyurethanes, polyureas, polyamides, carbamate functional polymers, polyisocyanates different from curing agent (c), blocked polyisocyanates different from curing agent (c), polyepoxides

15 different from curing agent (c), polyethers, polyacids different from curing agent (c), polyamines, polyanhydrides and copolymers and mixtures of the foregoing.

Nonlimiting examples of suitable hydroxyl group-containing polymers include acrylic polyols, polyester polyols, polyurethane polyols, polyether polyols, and mixtures of any of the foregoing. The hydroxyl group-containing polymer can

20 be an acrylic polyol that can have a hydroxyl equivalent weight ranging from 1000 to 100 grams per solid equivalent. The term "equivalent weight" is a calculated value based on the relative amounts of the various ingredients used in making the specified material and is based on the solids of the specified material. The relative amounts are those that result in the theoretical weight in grams of the

25 material like a polymer produced from the ingredients and give a theoretical number of the particular functional group that is present in the resulting polymer. The theoretical polymer weight is divided by the theoretical number to give the equivalent weight. For example, hydroxyl equivalent weight is based on the equivalents of reactive pendant and/or terminal hydroxyl groups in the hydroxyl-

30 containing polymer.

- Suitable hydroxyl group and/or carboxyl group-containing acrylic polymers can be prepared from polymerizable ethylenically unsaturated monomers and can be copolymers of (meth)acrylic acid and/or hydroxylalkyl esters of (meth)acrylic acid with one or more other polymerizable ethylenically unsaturated monomers
- 5 such as, for example alkyl esters of (meth)acrylic acid including methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate and 2-ethyl hexylacrylate, and vinyl aromatic compounds such as, for example styrene, alpha-methyl styrene, and vinyl toluene. As used herein, "(meth)acrylate" and like terms are intended to include both acrylates and methacrylates.
- 10 The acrylic polymer can be prepared from ethylenically unsaturated, beta-hydroxy ester functional monomers. Such monomers can be derived from the reaction of an ethylenically unsaturated acid functional monomer, such as monocarboxylic acids, for example acrylic acid, and an epoxy compound which does not participate in the free radical initiated polymerization with the unsaturated acid monomer. Nonlimiting examples of such epoxy compounds are glycidyl ethers and esters. Nonlimiting examples of suitable glycidyl ethers comprise glycidyl ethers of alcohols and phenols such as butyl glycidyl ether, octyl glycidyl ether, phenyl glycidyl ether, and the like. Nonlimiting examples of suitable glycidyl esters include those which are commercially available from Shell Chemical
- 15 15 Company under the tradename CARDURA E and from Exxon Chemical Company under the tradename GLYDEXX-10. Alternatively, the beta-hydroxy ester functional monomers are prepared from an ethylenically unsaturated, epoxy functional monomer, for example glycidyl (meth)acrylate and allyl glycidyl ether, and a saturated carboxylic acid, such as a saturated monocarboxylic acid, for example isostearic acid.
- 20 Epoxy functional groups can be incorporated into the polymer prepared from polymerizable ethylenically unsaturated monomers by copolymerizing oxirane group-containing monomers, for example glycidyl (meth)acrylate and allyl glycidyl ether, with other polymerizable ethylenically unsaturated monomers such
- 25 25 as those discussed above. Preparation of such epoxy functional acrylic polymers
- 30

is described in detail in U.S. Patent No. 4,001,156 at columns 3 to 6, which columns are specifically incorporated herein by reference.

- Carbamate functional groups can be incorporated into the polymer prepared from polymerizable ethylenically unsaturated monomers by
- 5 copolymerizing, for example the above-described ethylenically unsaturated monomers with a carbamate functional vinyl monomer such as a carbamate functional alkyl ester of methacrylic acid. Useful carbamate functional alkyl esters can be prepared by reacting, for example a hydroxyalkyl carbamate (which can be the reaction product of ammonia and ethylene carbonate or propylene carbonate)
 - 10 with methacrylic anhydride.

Other useful carbamate functional vinyl monomers include, for instance, the reaction product of hydroxyethyl methacrylate, isophorone diisocyanate, and hydroxypropyl carbamate; or the reaction product of hydroxypropyl methacrylate, isophorone diisocyanate, and methanol. Still other carbamate functional vinyl monomers may be used, such as the reaction product of isocyanic acid (HNCO) with a hydroxyl functional acrylic or methacrylic monomer such as hydroxyethyl acrylate, and those monomers described in U.S. Patent No. 3,479,328, which is incorporated herein by reference.

- Carbamate functional groups also can be incorporated into the acrylic polymer by reacting a hydroxyl functional acrylic polymer with a low molecular weight alkyl carbamate such as methyl carbamate. Pendent carbamate groups also can be incorporated into the acrylic polymer by a "transcarbamoylation" reaction in which a hydroxyl functional acrylic polymer is reacted with a low molecular weight carbamate derived from an alcohol or a glycol ether. The carbamate groups can exchange with the hydroxyl groups to yield the carbamate functional acrylic polymer and the original alcohol or glycol ether. Also, hydroxyl functional acrylic polymers can be reacted with isocyanic acid to provide pendent carbamate groups. Likewise, hydroxyl functional acrylic polymers can be reacted with urea to provide pendent carbamate groups.

30 The polymers prepared from polymerizable ethylenically unsaturated monomers can be prepared by solution polymerization techniques, which are well-

known to those skilled in the art, in the presence of suitable catalysts such as organic peroxides or azo compounds, for example benzoyl peroxide or N,N-azobis(isobutyronitrile). The polymerization can be carried out in an organic solution in which the monomers are soluble by techniques conventional in the art.

- 5 Alternatively, these polymers can be prepared by aqueous emulsion or dispersion polymerization techniques which are well-known in the art. The ratio of reactants and reaction conditions are selected to result in an acrylic polymer with the desired pendent functionality.

Polyester polymers also are useful in the coating compositions of the
10 invention as the additional polymer. Useful polyester polymers can comprise the condensation products of polyhydric alcohols and polycarboxylic acids.

Nonlimiting examples of suitable polyhydric alcohols include ethylene glycol, neopentyl glycol, trimethylol propane, and pentaerythritol. Nonlimiting examples of suitable polycarboxylic acids include adipic acid, 1,4-cyclohexyl dicarboxylic
15 acid, and hexahydrophthalic acid. Besides the polycarboxylic acids mentioned above, functional equivalents of the acids such as anhydrides where they exist or lower alkyl esters of the acids such as the methyl esters can be used. Also, small amounts of monocarboxylic acids such as stearic acid can be used. The ratio of reactants and reaction conditions are selected to result in a polyester polymer with
20 the desired pendent functionality, i.e., carboxyl or hydroxyl functionality.

For example hydroxyl group-containing polyesters can be prepared by reacting an anhydride of a dicarboxylic acid such as hexahydrophthalic anhydride with a diol such as neopentyl glycol in a 1:2 molar ratio. Where it is desired to enhance air-drying, suitable drying oil fatty acids may be used and can include
25 those derived from linseed oil, soya bean oil, tall oil, dehydrated castor oil, or tung oil.

Carbamate functional polyesters can be prepared by first forming a hydroxyalkyl carbamate that can be reacted with the polyacids and polyols used in forming the polyester. Alternatively, terminal carbamate functional groups can be
30 incorporated into the polyester by reacting isocyanic acid with a hydroxy functional polyester. Also, carbamate functionality can be incorporated into the polyester by

reacting a hydroxyl polyester with a urea. Additionally, carbamate groups can be incorporated into the polyester by a transcarbamoylation reaction. Preparation of suitable carbamate functional group-containing polyesters are those described in U.S. Patent No. 5,593,733 at column 2, line 40 to column 4, line 9, which portion
5 is incorporated herein by reference.

Polyurethane polymers containing terminal isocyanate (which can be blocked) or hydroxyl groups also can be used as the additional polymer in the coating compositions of the invention. The polyurethane polyols or NCO-terminated polyurethanes which can be used are those prepared by reacting
10 polyols including polymeric polyols with polyisocyanates. Polyureas containing terminal isocyanate or primary and/or secondary amine groups which also can be used can be those prepared by reacting polyamines including, but not limited to, polymeric polyamines with polyisocyanates.

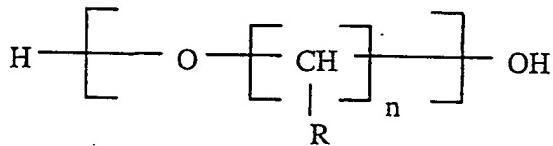
The hydroxyl/isocyanate or amine/isocyanate equivalent ratio can be
15 adjusted and reaction conditions can be selected to obtain the desired terminal groups. Nonlimiting examples of suitable polyisocyanates include those described in U.S. Patent No. 4,046,729 at column 5, line 26 to column 6, line 28, which portion is incorporated herein by reference. Nonlimiting examples of suitable polyols include those described in U.S. Patent No. 4,046,729 at column 7, line 52
20 to column 10, line 35, which portion is incorporated herein by reference.

Nonlimiting examples of suitable polyamines include those described in U.S. Patent No. 4,046,729 at column 6, line 61 to column 7, line 32 and in U.S. Patent No. 3,799,854 at column 3, lines 13 to 50, the indicated portions of both are incorporated herein by reference.

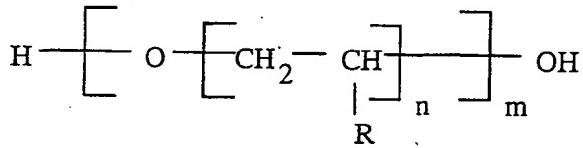
25 Carbamate functional groups can be introduced into the polyurethane polymers by reacting a polyisocyanate with a polyester having hydroxyl functionality and containing pendent carbamate groups. Alternatively, the polyurethane can be prepared by reacting a polyisocyanate with a polyester polyol and a hydroxyalkyl carbamate or isocyanic acid as separate reactants.
30 Nonlimiting examples of suitable polyisocyanates include aromatic isocyanates, (such as 4,4'-diphenylmethane diisocyanate, 1,3-phenylene diisocyanate, and

toluene diisocyanate), and aliphatic polyisocyanates (such as 1,4-tetramethylene diisocyanate, and 1,6-hexamethylene diisocyanate). Cycloaliphatic diisocyanates, such as, for example 1,4-cyclohexyl diisocyanate and isophorone diisocyanate can be employed.

- 5 Nonlimiting examples of suitable polyether polyols include polyalkylene ether polyols such as those having the following structural formulas (VII) or (VIII):
 (VII)



- 10 or (VIII)

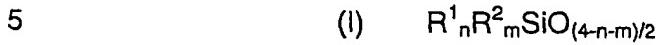


- wherein the substituent group R represents hydrogen or a lower alkyl group of 1 to 5 carbon atoms including mixed substituents, n has a value ranging from 2 to 6, and m has a value ranging from 8 to 100 or higher. Nonlimiting examples of
 15 polyalkylene ether polyols include poly(oxytetramethylene) glycols, poly(oxytetraethylene) glycols, poly(oxy-1,2-propylene) glycols, and poly(oxy-1,2-butylene) glycols.

- Also useful can be polyether polyols formed from oxyalkylation of various polyols, for example but not limited to, glycols such as ethylene glycol, 1,6-
 20 hexanediol, Bisphenol A, and the like, or other higher polyols such as trimethylolpropane, pentaerythritol, and the like. Polyols of higher functionality which can be utilized as indicated can be made, for instance, by oxyalkylation of compounds such as sucrose or sorbitol. One oxyalkylation method that can be used is reaction of a polyol with an alkylene oxide, including but not limited to,
 25 propylene or ethylene oxide, in the presence of an acidic or basic catalyst. Specific, nonlimiting examples of polyethers include those sold under the names TERATHANE and TERACOL, available from E. I. duPont de Nemours and Co.,

Inc.

In one embodiment, the second material can comprise at least one polysiloxane having at least one thermally curable group. The at least one polysiloxane has at least one of the following structural units (I) :



wherein each substituent group R^1 , which may be identical or different, represents a group selected from H, OH, a monovalent hydrocarbon group, and a monovalent siloxane group; each substituent group R^2 , which may be identical or different, represents a group comprising at least one reactive functional group.

10 It should be understood that the "at least one polysiloxane having at least one structural unit (I)" above is a polymer that contains at least two Si atoms per molecule. As used herein, the term "polymer" is meant to encompass oligomer, and includes without limitation both homopolymers and copolymers. It should also be understood that the at least one polysiloxane can include linear, branched,
15 dendritic or cyclic polysiloxanes.

Also, as used herein, the term "reactive" refers to a functional group that forms a covalent bond with another functional group under conditions sufficient to cure the composition.

Each of m and n depicted in the at least one structural unit (I) above fulfill
20 the requirements of $0 < n < 4$, $0 < m < 4$ and $2 \leq (m+n) < 4$. When $(m+n)$ is 3, the value represented by n can be 2 and the value represented by m is 1. Likewise, when $(m+n)$ is 2, the value represented by each of n and m is 1.

As used herein, a "monovalent hydrocarbon group" means a monovalent group having a backbone repeat unit based exclusively on carbon. As used
25 herein, "monovalent" refers to a substituent group that, as a substituent group, forms only one single, covalent bond. For example a monovalent group on the at least one polysiloxane will form one single covalent bond to a silicon atom in the backbone of the at least one polysiloxane polymer. As used herein, "hydrocarbon groups" are intended to encompass both branched or unbranched hydrocarbon
30 groups.

Thus, when referring to a "monovalent hydrocarbon group," the hydrocarbon group can be branched or unbranched, acyclic or cyclic, saturated or unsaturated, or aromatic, and can contain from 1 to 24 (or in the case of an aromatic group from 3 to 24) carbon atoms. Nonlimiting examples of such

- 5 hydrocarbon groups include alkyl, alkoxy, aryl, alkaryl, and alkoxyaryl groups. Nonlimiting examples of lower alkyl groups include, for example methyl, ethyl, propyl, and butyl groups. As used herein, "lower alkyl" refers to alkyl groups having from 1 to 6 carbon atoms. One or more of the hydrogen atoms of the hydrocarbon can be substituted with heteroatoms. As used herein, "heteroatoms"
- 10 means elements other than carbon, for example oxygen, nitrogen, and halogen atoms.

As used herein, "siloxane" means a group comprising a backbone comprising two or more -SiO- groups. For example, the siloxane groups represented by R¹, which is discussed above, and R, which is discussed below,

- 15 can be branched or unbranched, and linear or cyclic. The siloxane groups can be substituted with pendant organic substituent groups, for example alkyl, aryl, and alkaryl groups. The organic substituent groups can be substituted with heteroatoms, for example oxygen, nitrogen, and halogen atoms, reactive functional groups, for example those reactive functional groups discussed above
- 20 with reference to R², and mixtures of any of the foregoing.

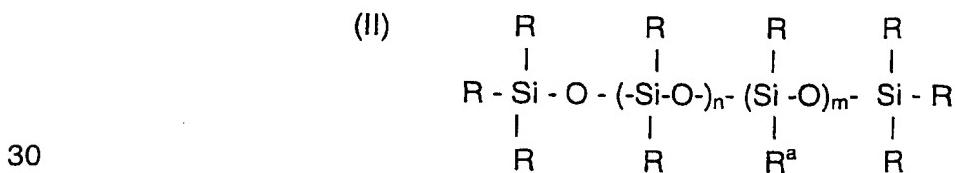
In another embodiment, each substituent group R², which may be identical or different, represents a group comprising at least one reactive functional group selected from a hydroxyl group, a carboxyl group, an isocyanate group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group such as an acrylate group and a methacrylate group, a maleimide group, a fumarate group, an onium salt group such as a sulfonium group and an ammonium group, an anhydride group, a hydroxy alkylamide group, and an epoxy group; wherein m and n fulfill the requirements of 0<n<4, 0<m<4

25 and 2≤(m+n)<4.

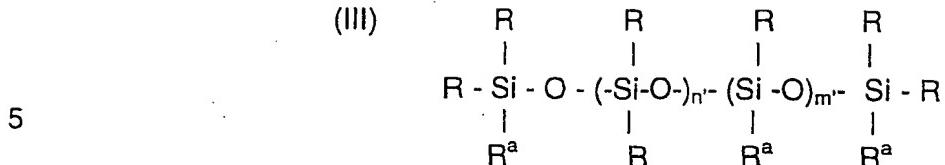
In one embodiment, the present invention is directed to a coating composition as previously described, wherein the at least one polysiloxane comprises at least two reactive functional groups. The at least one polysiloxane can have a reactive group equivalent weight ranging from 50 to 1000 mg per gram of the at least one polysiloxane. In one embodiment, the at least one polysiloxane has a hydroxyl group equivalent weight ranging from 50 to 1000 mg KOH per gram of the at least one polysiloxane. In another embodiment, the at least one polysiloxane has a hydroxyl group equivalent weight ranging from 100 to 300 mg KOH per gram of the at least one polysiloxane, while in another embodiment, the hydroxyl group equivalent weight ranges from 100 to 500 mg KOH per gram. The hydroxyl equivalent weight of the at least one polysiloxane may range between any combination of these values inclusive of the recited values.

In another embodiment, the present invention is directed to a coating composition as previously described, wherein at least one R² group represents a group comprising at least one reactive functional group selected from a hydroxyl group and a carbamate group. In yet another embodiment, the present invention is directed to a coating composition as previously described, wherein at least one R² group represents a group comprising at least two reactive functional groups selected from a hydroxyl group and a carbamate group. In another embodiment, the present invention is directed to a coating composition as previously described, wherein at least one R² group represents a group comprising an oxyalkylene group and at least two hydroxyl groups.

In one embodiment, the present invention is directed to a cured composition as previously described, wherein the at least one polysiloxane has the following structure (II) or (III):



or



- wherein: m has a value of at least 1; m' ranges from 0 to 75; n ranges from 0 to 75; n' ranges from 0 to 75; each R, which may be identical or different, is selected from H, OH, a monovalent hydrocarbon group, a monovalent siloxane group, and mixtures of any of the foregoing; and -R^a comprises the following structure (IV):
- 10 (IV) - R³-X

- wherein -R³ is selected from an alkylene group, an oxyalkylene group, an alkylene aryl group, an alkenylene group, an oxyalkenylene group, and an alkenylene aryl group; and X represents a group which comprises at least one reactive functional group selected from a hydroxyl group, a carboxyl group, an isocyanate group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group such as an acrylate group and a methacrylate group, a maleimide group, a fumarate group, an onium salt group such as a sulfonium group and an ammonium group, an anhydride group, a hydroxy alkylamide group, and an epoxy group.

- As used herein, "alkylene" refers to an acyclic or cyclic, saturated hydrocarbon group having a carbon chain length of from C₂ to C₂₅. Nonlimiting examples of suitable alkylene groups include, but are not limited to, those derived from propenyl, 1-butenyl, 1-pentenyl, 1-decenyl, and 1-heneicosenyl, such as, for example (CH₂)₃, (CH₂)₄, (CH₂)₅, (CH₂)₁₀, and (CH₂)₂₃, respectively, as well as isoprene and myrcene.
- As used herein, "oxyalkylene" refers to an alkylene group containing at least one oxygen atom bonded to, and interposed between, two carbon atoms and having an alkylene carbon chain length of from C₂ to C₂₅. Nonlimiting examples of suitable oxyalkylene groups include those derived from trimethylolpropane

monoallyl ether, trimethylolpropane diallyl ether, pentaerythritol monoallyl ether, polyethoxylated allyl alcohol, and polypropoxylated allyl alcohol, such as -(CH₂)₃OCH₂C(CH₂OH)₂(CH₂CH₂-).

As used herein, "alkylene aryl" refers to an acyclic alkylene group

- 5 substituted with at least one aryl group, for example, phenyl, and having an alkylene carbon chain length of C₂ to C₂₅. The aryl group can be further substituted, if desired. Nonlimiting examples of suitable substituent groups for the aryl group include, but are not limited to, hydroxyl groups, benzyl groups, carboxylic acid groups, and aliphatic hydrocarbon groups. Nonlimiting examples
- 10 of suitable alkylene aryl groups include, but are not limited to, those derived from styrene and 3-isopropenyl- α,ω -dimethylbenzyl isocyanate, such as -(CH₂)₂C₆H₄- and -CH₂CH(CH₃)C₆H₃(C(CH₃)₂(NCO). As used herein, "alkenylene" refers to an acyclic or cyclic hydrocarbon group having one or more double bonds and having an alkenylene carbon chain length of C₂ to C₂₅. Nonlimiting examples of suitable
- 15 alkenylene groups include those derived from propargyl alcohol and acetylenic diols, for example, 2,4,7,9-tetramethyl-5-decyne-4,7-diol which is commercially available from Air Products and Chemicals, Inc. of Allentown, Pennsylvania as SURFYNOL 104.

Formulae (II) and (III) are diagrammatic, and are not intended to imply that

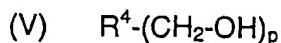
- 20 the parenthetical portions are necessarily blocks, although blocks may be used where desired. In some cases the polysiloxane may comprise a variety of siloxane units. This is increasingly true as the number of siloxane units employed increases, and especially true when mixtures of a number of different siloxane units are used. In those instances where a plurality of siloxane units are used and
- 25 it is desired to form blocks, oligomers can be formed which can be joined to form the block compound. By judicious choice of reactants, compounds having an alternating structure or blocks of alternating structure may be used.

- In one embodiment, the present invention is directed to a coating composition comprising the polysiloxane as previously described in which the
- 30 substituent group R³ represents an oxyalkylene group. In another embodiment,

R^3 represents an oxyalkylene group, and X represents a group which comprises at least two reactive functional groups.

- In another embodiment, the present invention is directed to any coating composition prepared from components as previously described comprising at least one polysiloxane having the structure (II) or (III) described above, wherein $(n + m)$ ranges from 2 to 9. In yet another embodiment, the components can comprise at least one polysiloxane having the structure (II) or (III) described above, $(n + m)$ ranges from 2 to 3. In another embodiment, the components can comprise at least one polysiloxane having the structure (II) or (III) described above, $(n' + m')$ ranges from 2 to 9. In another embodiment, the components can comprise at least one polysiloxane having the structure (II) or (III) described above, $(n' + m')$ ranges from 2 to 3.

- In one embodiment, the present invention is directed to any coating composition as previously described in which the components comprise at least one polysiloxane in which X represents a group comprising at least one reactive functional group selected from a hydroxyl group and a carbamate group. In another embodiment, the present invention is directed to polysiloxane as a component as previously described wherein X represents a group which comprises at least two hydroxyl groups. In yet another embodiment, the present invention is directed to polysiloxane as a component as previously described wherein X represents a group which comprises at least one group selected from H, a monohydroxy-substituted organic group, and a group having the following structure (V):



25

wherein the substituent group R^4 represents $-CH_2-C-$ R^3

30

when p is 2 and the substituent group R^3 represents a C_1 to C_4 alkylene group, or

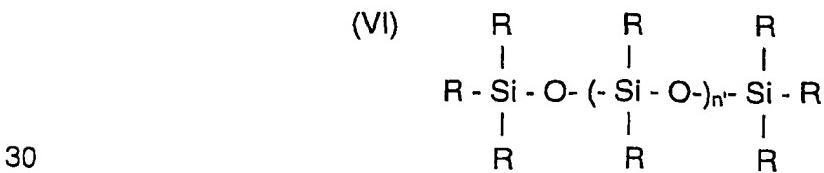
the substituent group R^4 represents $-CH_2-C-$ when p is 3,

wherein at least a portion of X represents a group having the structure (V). In another embodiment, the present invention is directed to any cured composition as previously described wherein m is 2 and p is 2.

In an embodiment of the present invention, the at least one polysiloxane is 5 nonreactive with the particles. In yet another embodiment, the present invention is directed to any coating composition as previously described, wherein the particles are different from the at least one polysiloxane. In yet another embodiment, the present invention is directed to any coating composition as previously described, wherein the particles have an average particle size less than 10 100 nanometers prior to incorporation into the cured composition. Methods known to one of ordinary skill in the art for measuring the average particle size are discussed in detail below.

In one embodiment, the present invention is directed to any coating composition as previously described comprising at least one polysiloxane having 15 the structure (II) or (III), wherein, if no curing agent is present, and if the at least one polysiloxane is a partial condensate of a silanol, then less than 70% by weight of the partial condensate is formed from $\text{CH}_3\text{Si}(\text{OH})_3$. These components used in these various embodiments can be selected from the coating components discussed above, and additional components also can be selected from those 20 recited above.

In another embodiment, the present invention is directed to any coating composition as previously described, wherein the components from which the composition is formed comprise at least one polysiloxane which is the reaction product of at least the following reactants: (i) at least one polysiloxane of the 25 formula (VI):



wherein each substituent group R, which may be identical or different, represents a group selected from H, OH, a monovalent hydrocarbon group, a

monovalent siloxane group, and mixtures of any of the foregoing; at least one of the groups represented by R is H, and n' ranges from 0 to 100, also can range from 0 to 10, and can further range from 0 to 5, such that the percent of SiH content of the polysiloxane ranges from 2 to 50 percent, and can range from 5 to 5 25 percent; and (ii) at least one molecule which comprises at least one functional group selected from a hydroxyl group, a carboxyl group, an isocyanate group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group such as an acrylate group and a methacrylate 10 group, a maleimide group, a fumarate group, an onium salt group such as a sulfonium group and an ammonium group, an anhydride group, a hydroxy alkylamide group, and an epoxy group and at least one unsaturated bond capable of undergoing a hydrosilylation reaction. In another embodiment, the at least one functional group is selected from hydroxyl groups.

15 It should be appreciated that the various R groups can be the same or different, and, in certain embodiments, the R groups will be entirely monovalent hydrocarbon groups or will be a mixture of different groups such as monovalent hydrocarbon groups and hydroxyl groups.

In another embodiment, this reaction product is ungelled. As used herein, 20 "ungelled" refers to a reaction product that is substantially free of crosslinking and has an intrinsic viscosity when dissolved in a suitable solvent, as determined, for example in accordance with ASTM-D1795 or ASTM-D4243. The intrinsic viscosity of the reaction product is an indication of its molecular weight. A gelled reaction product, on the other hand, since it is of an extremely high molecular 25 weight, will have an intrinsic viscosity too high to measure. As used herein, a reaction product that is "substantially free of crosslinking" refers to a reaction product that has a weight average molecular weight (Mw), as determined by gel permeation chromatography, of less than 1,000,000.

It also should be noted that the level of unsaturation contained in reactant 30 (ii) above, can be selected to obtain an ungelled reaction product. In other words, when a polysiloxane containing silicon hydride (i) having a higher average value of

Si-H functionality is used, reactant (ii) can have a lower level of unsaturation. For example the polysiloxane containing silicon hydride (i) can be a low molecular weight material where n' ranges from 0 to 5 and the average value of Si-H functionality is two or less. In this case, reactant (ii) can contain two or more

5 unsaturated bonds capable of undergoing hydrosilylation reaction without the occurrence of gelation.

Nonlimiting examples of polysiloxanes containing silicon hydride (i) include 1,1,3,3-tetramethyl disiloxane where n' is 0 and the average Si-H functionality is two; and polymethyl polysiloxane containing silicon hydride, where n' ranges from

10 4 to 5 and the average Si-H functionality is approximately two, such as is commercially available from BASF Corporation as MASILWAX BASE®.

Materials for use as reactant (ii) above can include hydroxyl functional group-containing allyl ethers such as those selected from trimethylolpropane monoallyl ether, pentaerythritol monoallyl ether, trimethylolpropane diallyl ether,

15 polyoxyalkylene alcohols such as polyethoxylated alcohol, polypropoxylated alcohol, and polybutoxylated alcohol, undecylenic acid-epoxy adducts, allyl glycidyl ether-carboxylic acid adducts, and mixtures of any of the foregoing. Mixtures of hydroxyl functional polyallyl ethers with hydroxyl functional monoallyl ethers or allyl alcohols are suitable as well. In certain instances, reactant (ii) can

20 contain at least one unsaturated bond in a terminal position. Reaction conditions and the ratio of reactants (i) and (ii) are selected so as to form the desired functional group.

The hydroxyl functional group-containing polysiloxane can be prepared by reacting a polysiloxane containing hydroxyl functional groups with an anhydride to

25 form the half-ester acid group under reaction conditions that favor only the reaction of the anhydride and the hydroxyl functional groups, and avoid further esterification from occurring. Nonlimiting examples of suitable anhydrides include hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, phthalic anhydride, trimellitic anhydride, succinic anhydride, chlorendic anhydride, alkenyl

30 succinic anhydride, and substituted alkenyl anhydrides such as octenyl succinic anhydride, and mixtures of any of the foregoing.

The half-ester group-containing reaction product thus prepared can be further reacted with a monoepoxide to form a polysiloxane containing secondary hydroxyl group(s). Nonlimiting examples of suitable monoépoxides are phenyl glycidyl ether, n-butyl glycidyl ether, cresyl glycidyl ether, isopropyl glycidyl ether, 5 glycidyl versatate, for example CARDURA E available from Shell Chemical Co., and mixtures of any of the foregoing.

In another embodiment, the present invention is directed to coating compositions as previously described wherein the components from which the coating compositions are formed comprise at least one polysiloxane which is a 10 carbamate functional group-containing polysiloxane which comprises the reaction product of at least the following reactants:

- (i) at least one polysiloxane containing silicon hydride of structure (VI) above where R and n' are as described above for that structure;
- (ii) at least one hydroxyl functional group-containing material having one or 15 more unsaturated bonds capable of undergoing hydrosilylation reaction as described above; and
- (iii) at least one low molecular weight carbamate functional material, comprising the reaction product of an alcohol or glycol ether and a urea.

Examples of such "low molecular weight carbamate functional material" 20 include, but are not limited to, alkyl carbamate and hexyl carbamates, and glycol ether carbamates described in U.S. Patent Nos. 5,922,475 and 5,976,701, which are incorporated herein by reference.

The carbamate functional groups can be incorporated into the polysiloxane by reacting the hydroxyl functional group-containing polysiloxane with the low 25 molecular weight carbamate functional material via a "transcarbamoylation" process. The low molecular weight carbamate functional material, which can be derived from an alcohol or glycol ether, can react with free hydroxyl groups of a polysiloxane polyol, that is, material having an average of two or more hydroxyl groups per molecule, yielding a carbamate functional polysiloxane and the original 30 alcohol or glycol ether. Reaction conditions and the ratio of reactants (i), (ii) and (iii) are selected so as to form the desired groups.

The low molecular weight carbamate functional material can be prepared by reacting the alcohol or glycol ether with urea in the presence of a catalyst such as butyl stannoic acid. Nonlimiting examples of suitable alcohols include lower molecular weight aliphatic, cycloaliphatic and aromatic alcohols, for example

- 5 methanol, ethanol, propanol, butanol, cyclohexanol, 2-ethylhexanol, and 3-methylbutanol. Nonlimiting examples of suitable glycol ethers include ethylene glycol methyl ether, and propylene glycol methyl ether. The incorporation of carbamate functional groups into the polysiloxane also can be achieved by reacting isocyanic acid with free hydroxyl groups of the polysiloxane.
- 10 As aforementioned, in addition to or in lieu of hydroxyl and/or carbamate functional groups, the at least one polysiloxane can contain one or more other reactive functional groups such as carboxyl groups, isocyanate groups, blocked isocyanate groups, carboxylate groups, primary and/or secondary amine groups, amide groups, urea groups, urethane groups, epoxy groups, and mixtures of any
- 15 of the foregoing.

When at least one polysiloxane contains carboxyl functional groups, the at least one polysiloxane can be prepared by reacting at least one polysiloxane containing hydroxyl functional groups as described above with a polycarboxylic acid or anhydride. Nonlimiting examples of polycarboxylic acids suitable for use

- 20 include adipic acid, succinic acid, and dodecanedioic acid. Nonlimiting examples of suitable anhydrides include those described above. Reaction conditions and the ratio of reactants are selected so as to form the desired functional groups.

In the case where at least one polysiloxane contains one or more isocyanate functional groups, the at least one polysiloxane can be prepared by

- 25 reacting at least one polysiloxane containing hydroxyl functional groups as described above with a polyisocyanate, such as a diisocyanate. Nonlimiting examples of suitable polyisocyanates include aliphatic polyisocyanates, such as, for example aliphatic diisocyanates, for example 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate; cycloaliphatic polyisocyanates, for example
- 30 1,4-cyclohexyl diisocyanate, isophorone diisocyanate, and α,α -xylylene diisocyanate; and aromatic polyisocyanates, for example 4,4'-diphenylmethane

diisocyanate, 1,3-phenylene diisocyanate, and tolylene diisocyanate. These and other suitable polyisocyanates are described in more detail in U.S. Patent No. 4,046,729, at column 5, line 26 to column 6, line 28, incorporated herein by reference. Reaction conditions and the ratio of reactants are selected so as to

5 form the desired functional groups.

- The substituent group X in structure (IV) can comprise a polymeric urethane or urea-containing material which is terminated with isocyanate, hydroxyl, primary or secondary amine functional groups, or mixtures of any of the foregoing. When the substituent group X comprises such functional groups, the at
- 10 least one polysiloxane can be the reaction product of at least one polysiloxane polyol as described above, one or more polyisocyanates and, optionally, one or more compounds having at least two active hydrogen atoms per molecule selected from hydroxyl groups, primary amine groups, and secondary amine groups.
- 15 Nonlimiting examples of suitable polyisocyanates are those described above. Nonlimiting examples of compounds having at least two active hydrogen atoms per molecule include polyols and polyamines containing primary and/or secondary amine groups.
- Nonlimiting examples of suitable polyols include polyalkylene ether polyols,
- 20 including thio ethers; polyester polyols, including polyhydroxy polyesteramides; and hydroxyl-containing polycaprolactones and hydroxy-containing acrylic interpolymers. Also useful are polyether polyols formed from the oxyalkylation of various polyols, for example glycols such as ethylene glycol, 1,6-hexanediol, Bisphenol A, and the like, or higher polyols such as trimethylolpropane,
- 25 pentaerythritol and the like. Polyester polyols also can be used. These and other suitable polyols are described in U.S. Patent No. 4,046,729 at column 7, line 52 to column 8, line 9; column 8, line 29 to column 9, line 66; and U.S. Patent No. 3,919,315 at column 2, line 64 to column 3, line 33, both incorporated herein by reference.
- 30 Nonlimiting examples of suitable polyamines include primary or secondary diamines or polyamines in which the groups attached to the nitrogen atoms can

- be saturated or unsaturated, aliphatic, alicyclic, aromatic, aromatic-substituted-aliphatic, aliphatic-substituted-aromatic and heterocyclic. Exemplary suitable aliphatic and alicyclic diamines include 1,2-ethylene diamine, 1,2-porphylene diamine, 1,8-octane diamine, isophorone diamine, propane-2,2-cyclohexyl amine, 5 and the like. Suitable aromatic diamines include phenylene diamines and the toluene diamines, for example o-phenylene diamine and p-tolylene diamine. These and other suitable polyamines are described in detail in U.S. Patent No. 4,046,729 at column 6, line 61 to column 7, line 26, incorporated herein by reference.
- 10 In one embodiment, the substituent group X of the structure (IV) can comprise a polymeric ester-containing group which is terminated with hydroxyl or carboxylic acid functional groups. When X is such a group, at least one polysiloxane can be the reaction product of one or more polysiloxane polyols as described above, one or more materials having at least one carboxylic acid 15 functional group, and one or more organic polyols. Nonlimiting suitable examples of materials having at least one carboxylic acid functional group include carboxylic acid group-containing polymers well-known in the art, for example carboxylic acid group-containing acrylic polymers, polyester polymers, and polyurethane polymers, such as those described in U.S. Patent No. 4,681,811. Nonlimiting 20 examples of suitable organic polyols include those described above.

To form the at least one polysiloxane containing epoxy groups, at least one polysiloxane containing hydroxyl functional groups as described above can be further reacted with a polyepoxide. The polyepoxide can be an aliphatic or cycloaliphatic polyepoxide or mixtures of any of the foregoing. Nonlimiting 25 examples of polyepoxides suitable for use include epoxy functional acrylic copolymers prepared from at least one ethylenically unsaturated monomer having at least one epoxy group, for example glycidyl (meth)acrylate and allyl glycidyl ether, and one or more ethylenically unsaturated monomers which have no epoxy functionality. The preparation of such epoxy functional acrylic copolymers is 30 described in detail in U.S. Patent No. 4,681,811 at column 4, line 52 to column 5, line 50, incorporated herein by reference. Reaction conditions and the ratio of

reactants are selected so as to form the desired functional groups.

In one embodiment, the present invention is directed to a coating composition as previously described in which the at least one polysiloxane comprises reactive functional groups which are thermally curable functional groups. In an alternative embodiment, at least one of the reactive functional groups of the polysiloxane can be curable by ionizing radiation or actinic radiation. In another alternative embodiment, the polysiloxane can comprise at least one functional group which is curable by thermal energy and at least one functional group which is curable by ionizing or actinic radiation. Suitable radiation curable groups are discussed in detail above.

The second material, when added to other components that form the coating composition, generally is present in the coating composition in an amount ranging from 0.5 to 98.5 weight percent based on total weight of the resin solids of the components which form the coating composition. In an embodiment of the present invention, the second material is generally present, when added to the other components forming the coating composition, in an amount of at least 25 percent by weight. The second material can be present in an amount of at least 5 percent by weight, and is typically present in an amount of at least 50 percent by weight based on total weight of the resin solids of the components which form the coating composition. Also the second material is generally present, when added to the other components in the coating composition, in an amount of less than 98.5 percent by weight. It can be present in an amount of less than 95 percent by weight, and is typically present in an amount of less than 90 percent by weight based on total weight of the resin solids of the components which form the coating composition. The amount of the second material present in the coating compositions may range between any combination of these values inclusive of the recited values.

In another embodiment, in lieu of or in addition to the first and second materials, one or more dual cure materials can be used to form the coating composition which comprise at least one functional group which is curable by thermal energy and at least one functional group which is curable by ionizing or

actinic radiation. Examples of such materials are disclosed above and in EP Application No. EP 940 422, which is incorporated herein by reference. When present, the dual cure material, when added to other components that form the coating composition, generally is present in the coating composition in an amount 5 ranging from 0.5 to 99 weight percent based on total weight of the resin solids of the components which form the coating composition, inclusive of the recited values.

In one embodiment, the components from which the coating composition is formed comprise at least one curing agent which is reactive with the thermally 10 curable group(s) of the second material. The at least one curing agent can be selected from aminoplast resins, polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing.

In another embodiment in which the dual cure material is present, the 15 components from which the coating composition is formed comprise at least one curing agent which is selected from polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing.

In another embodiment, the curing agent is an aminoplast. Aminoplast 20 resins, which comprise phenoplasts, as curing agents for hydroxyl, carboxylic acid, and carbamate functional group-containing materials are well known in the art. Suitable aminoplasts, such as, for example those discussed above, are known to those of ordinary skill in the art. Aminoplasts can be obtained from the condensation reaction of formaldehyde with an amine or amide. Nonlimiting 25 examples of amines or amides include melamine, urea, or benzoguanamine. Condensates with other amines or amides can be used; for example aldehyde condensates of glycoluril, which give a high melting crystalline product useful in powder coatings. While the aldehyde used is most often formaldehyde, other aldehydes such as acetaldehyde, crotonaldehyde, and benzaldehyde can be 30 used.

The aminoplast contains imino and methylol groups and in certain instances at least a portion of the methylol groups are etherified with an alcohol to modify the cure response. Any monohydric alcohol can be employed for this purpose including methanol, ethanol, n-butyl alcohol, isobutanol, and hexanol.

- 5 Nonlimiting examples of aminoplasts include melamine-, urea-, or benzoguanamine-formaldehyde condensates, in certain instances monomeric and at least partially etherified with one or more alcohols containing from one to four carbon atoms. Nonlimiting examples of suitable aminoplast resins are commercially available, for example from Cytec Industries, Inc. under the
- 10 trademark CYMEL®, and from Solutia, Inc. under the trademark RESIMENE®.

- In another embodiment, the present invention is directed to cured compositions as previously described wherein the aminoplast curing agent, when added to the other components which form the coating composition, is generally present in an amount ranging from 0.5 weight percent to 65 weight percent based
15 on total weight of the resin solids of the components which form the coating composition.

- Other curing agents suitable for use include, but are not limited to, polyisocyanate curing agents. As used herein, the term "polyisocyanate" is intended to include blocked (or capped) polyisocyanates as well as unblocked
20 polyisocyanates. The polyisocyanate can be an aliphatic or an aromatic polyisocyanate, or a mixture of the foregoing two. Diisocyanates can be used, although higher polyisocyanates such as isocyanurates of diisocyanates are often used. Higher polyisocyanates also can be used in combination with diisocyanates. Isocyanate prepolymers, for example reaction products of
25 polyisocyanates with polyols also can be used. Mixtures of polyisocyanate curing agents can be used.

- If the polyisocyanate is blocked or capped, any suitable aliphatic, cycloaliphatic, or aromatic alkyl monoalcohol known to those skilled in the art can be used as a capping agent for the polyisocyanate. Other suitable capping agents
30 include oximes and lactams. When used, the polyisocyanate curing agent is typically present, when added to the other components in the coating composition,

in an amount ranging from 5 to 65 weight percent, can be present in an amount ranging from 10 to 45 weight percent, and often are present in an amount ranging from 15 to 40 percent by weight based on the total weight of the resin solids of the components which form the coating composition.

- 5 Other useful curing agents comprise triazine derived isocyanates such as, for example the tricarbamoyl triazine compounds described in detail in U.S. Patent No. 5,084,541, which is incorporated by reference herein. When used, the triazine derived isocyanates can be present, when added to the other components in the coating composition, in an amount ranging up to 20 weight percent, and can
10 be present in an amount ranging from 1 to 20 weight percent, based on the total weight of the resin solids of the components which form the coating composition.

- Anhydrides as curing agents for hydroxyl functional group-containing materials also are well known in the art and can be used in the present invention. Nonlimiting examples of anhydrides suitable for use as curing agents in the
15 coating compositions of the invention include those having at least two carboxylic acid anhydride groups per molecule which are derived from a mixture of monomers comprising an ethylenically unsaturated carboxylic acid anhydride and at least one vinyl co-monomer, for example styrene, alpha-methyl styrene, vinyl toluene, and the like. Nonlimiting examples of suitable ethylenically unsaturated
20 carboxylic acid anhydrides include maleic anhydride, citraconic anhydride, and itaconic anhydride. Alternatively, the anhydride can be an anhydride adduct of a diene polymer such as maleinized polybutadiene or a maleinized copolymer of butadiene, for example a butadiene/styrene copolymer. These and other suitable anhydride curing agents are described in U.S. Patent No. 4,798,746 at column 10,
25 lines 16-50; and in U.S. Patent No. 4,732,790 at column 3, lines 41-57, both of which are incorporated herein by reference.

- Polyepoxides as curing agents for carboxylic acid functional group-containing materials are well known in the art. Nonlimiting examples of polyepoxides suitable for use in the coating compositions of the present invention
30 comprise polyglycidyl ethers of polyhydric phenols and of aliphatic alcohols, which can be prepared by etherification of the polyhydric phenol, or aliphatic alcohol with

an epihalohydrin such as epichlorohydrin in the presence of alkali. These and other suitable polyepoxides are described in U.S. Patent No. 4,681,811 at column 5, lines 33 to 58, which is incorporated herein by reference.

- Suitable curing agents for epoxy functional group-containing materials
- 5 comprise polyacid curing agents, such as the acid group-containing acrylic polymers prepared from an ethylenically unsaturated monomer containing at least one carboxylic acid group and at least one ethylenically unsaturated monomer which is free from carboxylic acid groups. Such acid functional acrylic polymers can have an acid number ranging from 30 to 150. Acid functional group-
10 containing polyesters can be used as well. The above-described polyacid curing agents are described in further detail in U.S. Patent No. 4,681,811 at column 6, line 45 to column 9, line 54, which is incorporated herein by reference.

- Also well known in the art as curing agents for isocyanate functional group-containing materials are polyols, that is, materials having two or more hydroxyl groups per molecule. Nonlimiting examples of such materials suitable for use in the coating compositions of the invention include polyalkylene ether polyols, including thio ethers; polyester polyols, including polyhydroxy polyesteramides; and hydroxyl-containing polycaprolactones and hydroxy-containing acrylic interpolymers. Also useful are polyether polyols formed from the oxyalkylation of
15 various polyols, for example glycols such as ethylene glycol, 1,6-hexanediol, Bisphenol A and the like, or higher polyols such as trimethylolpropane, pentaerythritol, and the like. Polyester polyols also can be used. These and other suitable polyol curing agents are described in U.S. Patent No. 4,046,729 at column 7, line 52 to column 8, line 9; column 8, line 29 to column 9, line 66; and
20 U.S. Patent No. 3,919,315 at column 2, line 64 to column 3, line 33, both of which are incorporated herein by reference.

- Polyamines also can be used as curing agents for isocyanate functional group-containing materials. Nonlimiting examples of suitable polyamine curing agents include primary or secondary diamines or polyamines in which the radicals
30 attached to the nitrogen atoms can be saturated or unsaturated, aliphatic, alicyclic, aromatic, aromatic-substituted-aliphatic, aliphatic-substituted -aromatic,

and heterocyclic. Nonlimiting examples of suitable aliphatic and alicyclic diamines include 1,2-ethylene diamine, 1,2-porphylene diamine, 1,8-octane diamine, isophorone diamine, propane-2,2-cyclohexyl amine, and the like. Nonlimiting examples of suitable aromatic diamines include phenylene diamines and the 5 toluene diamines, for example o-phenylene diamine and p-tolylene diamine. These and other suitable polyamines described in detail in U.S. Patent No. 4,046,729 at column 6, line 61 to column 7, line 26, which is incorporated herein by reference.

When desired, appropriate mixtures of curing agents may be used. It 10 should be mentioned that coating compositions can be formulated as a one-component coating composition where a curing agent such as an aminoplast resin and/or a triazine compound such as those described above is admixed with other coating composition components. The one-component coating composition can be storage stable as formulated. Alternatively, coating compositions can be . 15 formulated as a two-component coating composition where a polyisocyanate curing agent such as those described above can be added to a pre-formed admixture of the other coating composition components just prior to application. The pre-formed admixture can comprise curing agents such as aminoplast resins and/or triazine compounds such as those described above.

20 Generally, the curing agent, when added to other components that form the coating composition, is present in the coating composition in an amount ranging from 0.5 to 65 weight percent, can be present in an amount ranging from 1 to 20 weight percent, and also can be present in an amount ranging from 5 to 15 weight percent based on total weight of the resin solids of the components which form the 25 coating composition.

The components from which the coating composition is formed comprise a plurality of particles, wherein each component is different, that is, from the first and second material, dual cure materials (if present) and curing agents of the coating composition. The particles can be formed from materials selected from 30 polymeric and nonpolymeric inorganic materials, polymeric and nonpolymeric organic materials, composite materials, and mixtures of any of the foregoing. As

used herein, "formed from" denotes open, e.g., "comprising," claim language. As such, it is intended that a composition "formed from" a list of recited components be a composition comprising at least these recited components, and can further comprise other, nonrecited components, during the composition's formation.

- 5 As used herein, the term "polymeric inorganic material" means a polymeric material having a backbone repeat unit based on an element or elements other than carbon. For more information see James Mark et al., Inorganic Polymers, Prentice Hall Polymer Science and Engineering Series, (1992) at page 5, which is specifically incorporated by reference herein. Moreover, as used herein, the term
10 "polymeric organic materials" means synthetic polymeric materials, semisynthetic polymeric materials and natural polymeric materials, all of which have a backbone repeat unit based on carbon.

An "organic material," as used herein, means carbon containing compounds wherein the carbon is typically bonded to itself and to hydrogen, and often to other elements as well, and excludes binary compounds such as the carbon oxides, the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene, carbonyl sulfide, etc.; and carbon-containing ionic compounds such as metallic carbonates, for example calcium carbonate and sodium carbonate. See R. Lewis, Sr., Hawley's
20 Condensed Chemical Dictionary, (12th Ed. 1993) at pages 761-762, and M. Silberberg, Chemistry The Molecular Nature of Matter and Change (1996) at page 586, which are specifically incorporated by reference herein.

As used herein, the term "inorganic material" means any material that is not an organic material.

- 25 As used herein, the term "composite material" means a combination of two or more differing materials. The particles formed from composite materials generally have a hardness at their surface that is different from the hardness of the internal portions of the particle beneath its surface. More specifically, the surface of the particle can be modified in any manner well known in the art,
30 including, but not limited to, chemically or physically changing its surface characteristics using techniques known in the art.

For example a particle can be formed from a primary material that is coated, clad or encapsulated with one or more secondary materials to form a composite particle that has a softer surface. In yet another alternative embodiment, particles formed from composite materials can be formed from a 5 primary material that is coated, clad or encapsulated with a different form of the primary material. For more information on particles useful in the present invention, see G. Wypych, Handbook of Fillers, 2nd Ed. (1999) at pages 15-202, which are specifically incorporated by reference herein.

- The particles suitable for use in the coating compositions of the invention 10 can comprise inorganic elements or compounds known in the art. Suitable particles can be formed from ceramic materials, metallic materials, and mixtures of any of the foregoing. Suitable ceramic materials comprise metal oxides, metal nitrides, metal carbides, metal sulfides, metal silicates, metal borides, metal carbonates, and mixtures of any of the foregoing. Specific, nonlimiting examples 15 of metal nitrides are, for example boron nitride; specific, nonlimiting examples of metal oxides are, for example zinc oxide; nonlimiting examples of suitable metal sulfides are, for example molybdenum disulfide, tantalum disulfide, tungsten disulfide, and zinc sulfide; nonlimiting suitable examples of metal silicates are, for example aluminum silicates and magnesium silicates such as vermiculite.
- 20 The particles can comprise, for example a core of essentially a single inorganic oxide such as silica in colloidal, fumed, or amorphous form, alumina or colloidal alumina, titanium dioxide, cesium oxide, yttrium oxide, colloidal yttria, zirconia, e.g., colloidal or amorphous zirconia, and mixtures of any of the foregoing; or an inorganic oxide of one type upon which is deposited an organic 25 oxide of another type. It should be understood that when the cured composition of the invention is employed as a transparent topcoat, for example as a clearcoat in a multi-component composite coating composition, particles should not seriously interfere with the optical properties of the cured composition. As used herein, "transparent" means that the cured coating has a BYK Haze index of less than 50 30 as measured using a BYK/Haze Gloss instrument.

Nonpolymeric, inorganic materials useful in forming the particles of the present invention comprise inorganic materials selected from graphite, metals, oxides, carbides, nitrides, borides, sulfides, silicates, carbonates, sulfates, and hydroxides. A nonlimiting example of a useful inorganic oxide is zinc oxide.

- 5 Nonlimiting examples of suitable inorganic sulfides include molybdenum disulfide, tantalum disulfide, tungsten disulfide, and zinc sulfide. Nonlimiting examples of useful inorganic silicates include aluminum silicates and magnesium silicates, such as vermiculite. Nonlimiting examples of suitable metals include molybdenum, platinum, palladium, nickel, aluminum, copper, gold, iron, silver, alloys, and
10 mixtures of any of the foregoing.

In one embodiment, the present invention is directed to cured compositions as previously described wherein the particles are selected from fumed silica, amorphous silica, colloidal silica, alumina, colloidal alumina, titanium dioxide, cesium oxide, yttrium oxide, colloidal yttria, zirconia, colloidal zirconia, and

- 15 mixtures of any of the foregoing. In another embodiment, the present invention is directed to cured compositions as previously described wherein the particles include colloidal silica. As disclosed above, these materials can be surface treated or untreated.

- The coating composition can comprise precursors suitable for forming silica
- 20 particles in situ by a sol-gel process. The coating composition according to the present invention can comprise alkoxy silanes which can be hydrolyzed to form silica particles in situ. For example tetraethylortho silicate can be hydrolyzed with an acid such as hydrochloric acid and condensed to form silica particles. Other useful particles include surface-modified silicas such as are described in U.S.
25 Patent No. 5,853,809 at column 6, line 51 to column 8, line 43, which is incorporated herein by reference.

- In one embodiment of the present invention, the particles have a hardness value greater than the hardness value of materials that can abrade a polymeric coating or a polymeric substrate. Examples of materials that can abrade the
30 polymeric coating or polymeric substrate include, but are not limited to, dirt, sand, rocks, glass, carwash brushes, and the like. The hardness values of the particles

and the materials that can abrade the polymeric coating or polymeric substrate can be determined by any conventional hardness measurement method, such as Vickers or Brinell hardness, but also can be determined according to the original Mohs' hardness scale which indicates the relative scratch resistance of the

- 5 surface of a material on a scale of one to ten. The Mohs' hardness values of several nonlimiting examples of particles formed from inorganic materials suitable for use in the present invention are given in Table A below.

Table A

Particle material	Mohs' hardness (original scale)
Boron nitride	2 ¹
Graphite	0.5-1 ²
Molybdenum disulfide	1 ³
Talc	1-1.5 ⁴
Mica	2.8-3.2 ⁵
Kaolinite	2.0-2.56
Gypsum	1.6-2 ⁷
Calcite (calcium carbonate)	3 ⁸
Calcium fluoride	4 ⁹
zinc oxide	4.5 ¹⁰
Aluminum	2.5 ¹¹
Copper	2.5-3 ¹²
Iron	4-5 ¹³
Gold	2.5-3 ¹⁴
Nickel	5 ¹⁵
Palladium	4.8 ¹⁶
Platinum	4.3 ¹⁷
Silver	2.5-4 ¹⁸
Zinc sulfide	3.5-4 ¹⁹

¹ K. Ludema, Friction, Wear, Lubrication, (1996) at page 27, which is hereby incorporated by reference.

² R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22.

³ R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 793, which is hereby incorporated by reference.

⁴ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 1113, which is hereby incorporated by reference.

⁵ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 784, which is hereby incorporated by reference.

⁶ Handbook of Chemistry and Physics at page F-22.

⁷ Handbook of Chemistry and Physics at page F-22.

⁸ Friction, Wear, Lubrication at page 27.

⁹ Friction, Wear, Lubrication at page 27.

¹⁰ Friction, Wear, Lubrication at page 27.

¹¹ Friction, Wear, Lubrication at page 27.

¹² Handbook of Chemistry and Physics at page F-22.

¹³ Handbook of Chemistry and Physics at page F-22.

¹⁴ Handbook of Chemistry and Physics at page F-22.

¹⁵ Handbook of Chemistry and Physics at page F-22.

¹⁶ Handbook of Chemistry and Physics at page F-22.

¹⁷ Handbook of Chemistry and Physics at page F-22.

¹⁸ Handbook of Chemistry and Physics at page F-22.

¹⁹ R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 4-158.

In one embodiment, the Mohs' hardness value of the particles is greater than 5.

In certain embodiments, the Mohs' hardness value of the particles, such as silica, is greater than 6.

- As mentioned above, the Mohs' hardness scale relates to the resistance of
- 5 a material to scratching. The present invention therefore further contemplates particles that have a hardness at their surface that is different from the hardness of the internal portions of the particle beneath its surface. More specifically, and as discussed above, the surface of the particle can be modified in any manner well known in the art, including, but not limited to, chemically changing the
- 10 particle's surface characteristics using techniques known in the art such that the surface hardness of the particle is greater than the hardness of the materials that can abrade the polymeric coating or polymeric substrate while the hardness of the particle beneath the surface is less than the hardness of the materials that can abrade the polymeric coating or polymeric substrate.
- 15 As another alternative, a particle can be formed from a primary material that is coated, clad or encapsulated with one or more secondary materials to form a composite material that has a harder surface. Alternatively, a particle can be formed from a primary material that is coated, clad or encapsulated with a differing form of the primary material to form a composite material that has a
- 20 harder surface.

In one example, and without limiting the present invention, an inorganic particle formed from an inorganic material such as silicon carbide or aluminum nitride can be provided with a silica, carbonate or nanoclay coating to form a useful composite particle. In another nonlimiting example, a silane coupling agent

25 with alkyl side chains can interact with the surface of an inorganic particle formed from an inorganic oxide to provide a useful composite particle having a "softer" surface. Other examples include cladding, encapsulating or coating particles formed from nonpolymeric or polymeric materials with differing nonpolymeric or polymeric materials. A specific nonlimiting example of such composite particles is

30 DUALITE™, which is a synthetic polymeric particle coated with calcium carbonate

that is commercially available from Pierce and Stevens Corporation of Buffalo, NY.

- In one nonlimiting embodiment of the invention, the particles are formed from solid lubricant materials. As used herein, the term "solid lubricant" means
- 5 any solid used between two surfaces to provide protection from damage during relative movement and/or to reduce friction and wear. In one embodiment, the solid lubricants are inorganic solid lubricants. As used herein, "inorganic solid lubricant" means that the solid lubricants have a characteristic crystalline habit which causes them to shear into thin, flat plates which readily slide over one
- 10 another and thus produce an antifriction lubricating effect. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 712, which is specifically incorporated by reference herein. Friction is the resistance to sliding one solid over another. F. Clauss, Solid Lubricants and Self-Lubricating Solids (1972) at page 1, which is specifically incorporated by reference herein.
- 15 In one nonlimiting embodiment of the invention, the particles have a lamellar structure. Particles having a lamellar structure are composed of sheets or plates of atoms in hexagonal array, with strong bonding within the sheet and weak van der Waals bonding between sheets, providing low shear strength between sheets. A nonlimiting example of a lamellar structure is a hexagonal
- 20 crystal structure. Inorganic solid particles having a lamellar fullerene (i.e., buckyball) structure also are useful in the present invention.
- Nonlimiting examples of suitable materials having a lamellar structure that are useful in forming the particles of the present invention include boron nitride, graphite, metal dichalcogenides, mica, talc, gypsum, kaolinite, calcite, cadmium
- 25 iodide, silver sulfide, and mixtures of any of the foregoing. Suitable metal dichalcogenides include molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide, and mixtures of any of the foregoing.
- The particles can be formed from nonpolymeric, organic materials.
- 30 Nonlimiting examples of nonpolymeric, organic materials useful in the present

invention include, but are not limited to, stearates (such as zinc stearate and aluminum stearate), diamond, carbon black, and stearamide.

The particles can be formed from inorganic polymeric materials.

Nonlimiting examples of useful inorganic polymeric materials include

- 5 polyphosphazenes, polysilanes, polysiloxane, polygermanes, polymeric sulfur, polymeric selenium, silicones, and mixtures of any of the foregoing. A specific, nonlimiting example of a particle formed from an inorganic polymeric material suitable for use in the present invention is TOSPEARL²⁰, which is a particle formed from cross-linked siloxanes and is commercially available from Toshiba Silicones
- 10 Company, Ltd. of Japan.

The particles can be formed from synthetic, organic polymeric materials.

Nonlimiting examples of suitable organic polymeric materials include, but are not limited to, thermoset materials and thermoplastic materials. As used herein, a "thermoplastic" material is a material that softens when exposed to heat and

- 15 returns to its original condition when cooled to room temperature. Nonlimiting examples of suitable thermoplastic materials include thermoplastic polyesters such as polyethylene terephthalate, polybutylene terephthalate, and polyethylene naphthalate, polycarbonates, polyolefins such as polyethylene, polypropylene, and polyisobutene, acrylic polymers such as copolymers of styrene and an acrylic
- 20 acid monomer, and polymers containing methacrylate, polyamides, thermoplastic polyurethanes, vinyl polymers, and mixtures of any of the foregoing.

Nonlimiting examples of suitable thermoset materials include thermoset polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermoset polyurethanes, and mixtures of any of the foregoing. A specific, nonlimiting

- 25 example of a synthetic polymeric particle formed from an epoxy material is an epoxy microgel particle. As used herein, a "thermoset" material is a material that material solidifies or "sets" irreversibly when heated. A thermoset material has formed a crosslinked network. As used herein, a polymeric material is "crosslinked" if it at least partially forms a polymeric network. One skilled in the art

²⁰ See R. J. Perry "Applications for Cross-Linked Siloxane Particles" Chemtech, February 1999 at pages 39-44.

will understand that the presence and degree of crosslinking (crosslink density) can be determined by a variety of methods, such as dynamic mechanical thermal analysis (DMTA) using a TA Instruments DMA 2980 DMTA analyzer conducted under nitrogen such as is described above. This method determines the glass

5 transition temperature and crosslink density of free films of coatings or polymers. These physical properties of a cured material are related to the structure of the crosslinked network.

The particles also can be hollow particles formed from materials selected from polymeric and nonpolymeric inorganic materials, polymeric and nonpolymeric
10 organic materials, composite materials, and mixtures of any of the foregoing. Nonlimiting examples of suitable materials from which the hollow particles can be formed are described above. In one embodiment, the hollow particles are hollow glass spheres.

The particles according to the present invention that are applied to the
15 polymeric substrate or polymeric coating, for example but not limited to, the electrodeposited coating, the primer coating, or the topcoat, can be present in a dispersion, suspension or emulsion in a carrier. Nonlimiting examples of suitable carriers include, but are not limited to, water, solvents, surfactants, or a mixture of any of the foregoing. Nonlimiting examples of suitable solvents include, but are
20 not limited to, mineral oil, alcohols such as methanol or butanol, ketones such as methyl amyl ketone, aromatic hydrocarbons such as xylene, glycol ethers such as ethylene glycol monobutyl ether, esters, aliphatics, and mixtures of any of the foregoing.

Prior to incorporation, one class of particles which can be used according
25 to the present invention includes sols, such as an organosol, of the particles. These sols can be of a wide variety of small-particle, colloidal silicas having an average particle size in ranges such as identified above.

The colloidal silicas can be surface modified during or after the particles are initially formed. These surface modified silicas may contain on their surface
30 chemically bonded carbon-containing moieties, as well as such groups as anhydrous SiO₂ groups and SiOH groups, various ionic groups physically

associated or chemically bonded within the surface of the silica, adsorbed organic groups, or combinations of any of the foregoing, depending on the characteristics of the particular silica desired. Such surface modified silicas are described in detail in U.S. Patent No. 4,680,204, which is incorporated herein by reference.

- 5 Such materials can be prepared by a variety of techniques in various forms, nonlimiting examples comprise organosols and mixed sols. As used herein the term "mixed sols" is intended to include those dispersions of colloidal silica in which the dispersing medium comprises both an organic liquid and water. Such small particle colloidal silicas are readily available, are essentially colorless and
- 10 have refractive indices which permit their inclusion in compositions that, without additional pigments or components known in the art to color and/or decrease the transparency of such compositions, result in colorless, transparent coatings.

- Suitable nonlimiting examples of particles include colloidal silicas, such as those commercially available from Nissan Chemical Company under the
- 15 trademark ORGANOSILICASOLS™ such as ORGANOSILICASOL™ MT-ST, and from Clariant Corporation as HIGHLINK™; colloidal aluminas, such as those commercially available from Nalco Chemical under the trademark NALCO 8676®; and colloidal zirconias, such as those commercially available from Nissan Chemical Company under the trademark HIT-32M®.

- 20 The particles can be incorporated into the compositions of the invention in the form of a stable dispersion. When the particles are in a colloidal form, the dispersions can be prepared by dispersing the particles in a carrier under agitation and solvent that is present can be removed under vacuum at ambient temperatures. In certain embodiments, the carrier can be other than a solvent,
- 25 such as the surface active agents described in detail below, including, but not limited to a polysiloxane containing reactive functional groups, including, but not limited to, the at least one polysiloxane (a).

- 30 Alternatively, the dispersions can be prepared as described in U.S. Patent Nos. 4,522,958 or 4,526,910, which are incorporated by reference herein. The particles can be "cold-blended" with the at least one polysiloxane prior to incorporation into the inventive compositions. Alternatively, the particles can be

post-added to an admixture of any remaining composition components (including, but not limited to, the at least one polysiloxane (a)) and dispersed therein using dispersing techniques well-known in the art.

- When the particles are in other than colloidal form, for example but not limited to, agglomerate form, the dispersions can be prepared by dispersing the agglomerate in the carrier, for example but not limited to, the at least one polysiloxane (a), to stably disperse the particles therein. Dispersion techniques such as grinding, milling, microfluidizing, ultrasounding, or any other pigment dispersing techniques well known in the art of coatings formulation can be used.
- Alternatively, the particles can be dispersed by any other dispersion techniques known in the art. If desired, the particles in other than colloidal form can be post-added to an admixture of other composition components and dispersed therein using any dispersing techniques known in the art.

In one embodiment, the present invention is directed to compositions which comprise a plurality of particles, wherein a first portion of the particles is present in a surface region of the cured composition in a concentration which is higher than a concentration of a second portion of particles which is present in a bulk region of the cured composition.

- As used herein "surface region" of the cured composition means the region which is generally parallel to the exposed air-surface of the coated substrate and which has thickness generally extending perpendicularly from the surface of the cured coating to a depth ranging from at least 20 nanometers to 150 nanometers beneath the exposed surface. In certain embodiments, this thickness of the surface region ranges from at least 20 nanometers to 100 nanometers, and can range from at least 20 nanometers to 50 nanometers, inclusive of the recited values. As used herein, "bulk region" of the cured composition means the region which extends beneath the surface region and which is generally parallel to the surface of the coated substrate. The bulk region has a thickness extending from its interface with the surface region through the cured coating to the substrate or coating layer beneath the cured composition.

In embodiments of the present invention in which the particles have an average particle size greater than 50 nanometers, the thickness of the surface region generally extends perpendicularly from the surface of the cured coating to a depth equal to three times the average particle size of the particles, and this

5 surface can extend to a depth equal to two times the average particle size of the particles.

The concentration of particles in the cured composition can be characterized in a variety of ways. For example the average number density of particles (i.e., the average number or population of particles per unit volume)

10 dispersed in the surface region is greater than the average number density dispersed in the bulk region. Alternatively, the average volume fraction (i.e., volume occupied by particles / total volume) or average weight percent per unit volume, i.e., ((the weight of particles within a unit volume of cured coating) / (total weight of the unit volume of cured coating)) x 100% of the particles dispersed in

15 the surface region is greater than the average volume fraction or average weight percent of particles dispersed within the bulk region.

The concentration of particles (as characterized above) present in the surface region of the cured coating can be determined, if desired, by a variety of surface analysis techniques well known in the art, such as Transmission Electron Microscopy ("TEM"), Surface Scanning Electron Microscopy ("X-SEM"), Atomic Force Microscopy ("AFM"), and X-ray Photoelectron Spectroscopy.

For example the concentration of particles present in the surface region of the cured coating may be determined by cross-sectional transmission electron microscopy techniques. A useful transmission electron microscopy method is

25 described generally as follows. A coating composition is applied to a substrate and cured under conditions appropriate to the composition and substrate. Samples of the cured coating are then removed or delaminated from the substrate and embedded in a cured epoxy resin using techniques as are well known in the art. The embedded samples then can be microtomed at room temperature using

30 techniques well known in the art, such as by forming a block face. The sections can be cut using a 45° diamond knife edge mounted in a holder with a "boat

- cavity" to hold water. During the cutting process, sections float to the surface of the water in the boat cavity. Once a few cuts reach an interference color of bright to dark gold (i.e., approximately 100 to 150 nanometers thickness), individual samples typically are collected onto a formvar-carbon coated grid and dried at
- 5 ambient temperature on a glass slide. The samples are then placed in a suitable transmission electron microscope, such as a Philips CM12 TEM, and examined at various magnifications, such as at 105,000 X magnification, for documentation of particle concentration at the surface region, via electron micrography. The concentration of particles in a surface region of a cured coating can be
- 10 ascertained upon visual inspection of the electron micrograph.

It should be understood that the particles can be present in the surface region such that a portion of the particles at least partially protrudes above the cured coating surface, essentially unprotected by an organic coating layer.

Alternatively, the particles can be present in the surface region such that this

- 15 organic coating layer lies between the particles and the exposed air-surface interface of the surface region.

- In one embodiment, the present invention is directed to cured compositions as previously described wherein the particles have an average particle size less than 100 microns prior to incorporation into the coating composition, and can have
- 20 an average particle size less than 50 microns prior to incorporation into the coating composition. In another embodiment, the present invention is directed to cured compositions as previously described wherein the particles have an average particle size ranging from 1 to less than 1000 nanometers prior to incorporation into the coating composition. In another embodiment, the present
- 25 invention is directed to cured compositions as previously described wherein the particles have an average particle size ranging from 1 to 100 nanometers prior to incorporation into the coating composition.

- In another embodiment, the present invention is directed to cured compositions as previously described wherein the particles have an average
- 30 particle size ranging from 5 to 50 nanometers prior to incorporation into the composition. In another embodiment, the present invention is directed to cured

compositions as previously described wherein the particles have an average particle size ranging from 5 to 25 nanometers prior to incorporation into the composition. The particle size may range between any combination of these values inclusive of the recited values.

- 5 In an embodiment where the average particle size of the particles is greater than one micron, the average particle size can be measured according to known laser scattering techniques. For example the average particle size of such particles is measured using a Horiba Model LA 900 laser diffraction particle size instrument, which uses a helium-neon laser with a wave length of 633 nm to
- 10 measure the size of the particles and assumes the particle has a spherical shape, i.e., the "particle size" refers to the smallest sphere that will completely enclose the particle.

- In an embodiment of the present invention wherein the size of the particles is less than or equal to one micron, the average particle size can be determined
- 15 by visually examining an electron micrograph of a transmission electron microscopy ("TEM") image, measuring the diameter of the particles in the image, and calculating the average particle size based on the magnification of the TEM image. One of ordinary skill in the art will understand how to prepare such a TEM image, and a description of one such method is disclosed in the examples set
 - 20 forth below. In one nonlimiting embodiment of the present invention, a TEM image with 105,000X magnification is produced, and a conversion factor is obtained by dividing the magnification by 1000. Upon visual inspection, the diameter of the particles is measured in millimeters, and the measurement is converted to nanometers using the conversion factor. The diameter of the particle
 - 25 refers to the smallest diameter sphere that will completely enclose the particle.

- The shape (or morphology) of the particles can vary depending upon the specific embodiment of the present invention and its intended application. For example generally spherical morphologies (such as solid beads, microbeads, or hollow spheres), can be used, as well as particles that are cubic, platy, or acicular
- 30 (elongated or fibrous). Additionally, the particles can have an internal structure that is hollow, porous or void free, or a combination of any of the foregoing, e.g., a

hollow center with porous or solid walls. For more information on suitable particle characteristics see H. Katz et al. (Ed.), Handbook of Fillers and Plastics (1987) at pages 9-10, which are specifically incorporated by reference herein.

- It will be recognized by one skilled in the art that mixtures of one or more particles having different average particle sizes can be incorporated into the compositions in accordance with the present invention to impart the desired properties and characteristics to the compositions. For example particles of varying particle sizes can be used in the compositions according to the present invention.
- 10 In one embodiment, the present invention is directed to compositions as previously described wherein the particles, when added to the other components which form the composition, are present in the composition in an amount ranging from 0.01 to 75 weight percent based on total weight of the resin solids of the components which form the composition. In another embodiment, the present invention is directed to compositions as previously described wherein the particles, when added to the other components which form the composition, are present in the composition in an amount of at least 0.1 weight percent, can be present in the composition in an amount at least 0.5 weight percent, and also can be present in the composition in an amount greater than 5 weight percent based 20 on total weight of the resin solids of the components which form the composition.
- In yet another embodiment, the present invention is directed to cured compositions as previously described wherein, the particles, when added to the other components which form the composition, are present in the composition in an amount less than 75 weight percent based on total weight of the resin solids of the components which form the composition. In a further embodiment, the present invention is directed to compositions as previously described wherein the particles, when added to the other components which form the composition, are present in the composition in an amount less than 50 weight percent based on total weight of the resin solids of the components which form the composition. In 30 another embodiment, the present invention is directed to compositions as previously described wherein the particles, when added to the other components

- which form the composition, are present in the composition in an amount less than 20 weight percent based on total weight of the resin solids of the components which form the composition. In another embodiment, the present invention is directed to compositions as previously described wherein the particles, when
- 5 added to the other components which form the composition, are present in the composition in an amount less than 10 weight percent based on total weight of the resin solids of the components which form the composition. The amount of particles present may range between any combination of these values inclusive of the recited values.
- 10 Additionally, in another embodiment, the present invention is directed to compositions wherein at least one surface active agent can be present during the formation of the compositions as previously described. The at least one surface active agent can be selected from anionic, nonionic, and cationic surface active agents.
- 15 As used herein, by "surface active agent" is meant any material which tends to lower the solid surface tension or surface energy of the cured composition or coating. That is, the cured composition or coating formed from a composition comprising a surface active agent has a lower solid surface tension or surface energy than a cured coating formed from the analogous composition
- 20 which does not contain the surface active agent.
- For purposes of the present invention, solid surface tension can be measured according to the Owens-Wendt method using a Rame'-Hart Contact Angle Goniometer with distilled water and methylene iodide as reagents. Generally, a 0.02 cc drop of one reagent is placed upon the cured coating surface
- 25 and the contact angle and its complement are measured using a standard microscope equipped with the goniometer. The contact angle and its complement are measured for each of three drops. The process is then repeated using the other reagent. An average value is calculated for the six measurements for each of the reagents. The solid surface tension is then calculated using the Owens-
- 30 Wendt equation:

$$\{ \gamma_l (1 + \cos \Phi) \}/2 = (\gamma_l^d \gamma_s^d)^{1/2} + (\gamma_l^p \gamma_s^p)^{1/2}$$

where γ_l is the surface tension of the liquid (methylene iodide = 50.8, distilled water = 72.8) and γ^d and γ^p are the dispersion and polar components (methylene iodide γ^d = 49.5, γ^p = 1.3; distilled water γ^d = 21.8, γ^p = 51.0); the values for Φ measured and the $\cos \Phi$ determined. Two equations are then setup,

5 one for methylene iodide and one for water. The only unknowns are γ_s^d and γ_s^p . The two equations are then solved for the two unknowns. The two components combined represent the total solid surface tension.

- The at least one surface active agent can be selected from amphiphilic, reactive functional group-containing polysiloxanes, amphiphilic fluoropolymers, 10 and mixtures of any of the foregoing. With reference to water-soluble or water-dispersible amphiphilic materials, the term "amphiphilic" means a polymer having a generally hydrophilic polar end and a water-insoluble generally hydrophobic end. Nonlimiting examples of suitable functional group-containing polysiloxanes for use as surface active agents include those polysiloxanes described below.
- 15 Nonlimiting examples of suitable amphiphilic fluoropolymers include fluoroethylene-alkyl vinyl ether alternating copolymers (such as those described in U.S. Patent No. 4,345,057) available from Asahi Glass Company under the tradename LUMIFLON; fluorosurfactants, such as the fluoroaliphatic polymeric esters commercially available from 3M of St. Paul, Minnesota under the 20 tradename FLUORRAD; functionalized perfluorinated materials, such as 1H,1H-perfluoro-nonanol commercially available from FluoroChem USA; and perfluorinated (meth)acrylate resins.

Nonlimiting examples of other surface active agents suitable for use in the cured composition or coating of the present invention can include anionic, 25 nonionic and cationic surface active agents. Nonlimiting examples of suitable anionic surface active agents include sulfates or sulfonates. Specific nonlimiting examples include higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group and a straight- or branched-chain, e.g., the sodium salts of decyl, undecyl, 30 dodecyl, tridecyl, tetradecyl, pentadecyl or hexadecyl benzene sulfonate and the higher alkyl toluene, xylene and phenol sulfonates; alkyl naphthalene sulfonate,

and sodium dinonyl naphthalene sulfonate. Other nonlimiting examples of suitable anionic surface active agents include olefin sulfonates, including long chain alkenylene sulfonates, long chain hydroxyalkane sulfonates, and mixtures of any of the foregoing. Nonlimiting examples of other sulfate or sulfonate

- 5 detergents are paraffin sulfonates such as the reaction products of alpha olefins and bisulfites (e.g., sodium bisulfite). Also comprised are sulfates of higher alcohols, such as sodium lauryl sulfate, sodium tallow alcohol sulfate, or sulfates of mono- or di-glycerides of fatty acids (e.g., stearic monoglyceride monosulfate), alkyl poly(ethoxy)ether sulfates including, but not limited to, the sulfates of the
- 10 condensation products of ethylene oxide and lauryl alcohol (usually having 1-5 ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ether sulfonates; aromatic poly(ethenoxy)ether sulfates including, but not limited to, the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having 1-20 oxyethylene groups per molecule).
- 15 Further nonlimiting examples include salts of sulfated aliphatic alcohol, alkyl ether sulfate and/or alkyl aryl ethoxy sulfate available from Rhone-Poulenc - under the general tradename ABEX. Phosphate mono- or di-ester type anionic surface active agents also can be used. These anionic surface active agents are well known in the art and are commercially available under the general trademark
- 20 GAFAC from GAF Corporation and under the general trademark TRITON from Rohm & Haas Company.

Nonlimiting examples of nonionic surface active agents suitable for use in the cured composition or coating of the present invention include those containing ether linkages and which are represented by the following general formula:

- 25 RO(R'O)_nH; wherein the substituent group R represents a hydrocarbon group containing 6 to 60 carbon atoms, the substituent group R' represents an alkylene group containing 2 or 3 carbon atoms, and mixtures of any of the foregoing, and n is an integer ranging from 2 to 100.

Such nonionic surface active agents can be prepared by treating fatty

- 30 alcohols or alkyl-substituted phenols with an excess of ethylene or propylene oxide. The alkyl carbon chain may contain from 14 to 40 carbon atoms and may

be derived from a long chain fatty alcohol such as oleyl alcohol or stearyl alcohol. Nonionic polyoxyethylene surface active agents of the type represented by the formula above are commercially available under the general trade designation SURFYNOL from Air Products Chemicals, Inc.; PLURONIC or TETRONIC from 5 BASF Corporation; TERGITOL from Union Carbide; and SURFONIC from Huntsman Corporation. Other nonlimiting examples of suitable nonionic surface active agents include block copolymers of ethylene oxide and propylene oxide based on a glycol such as ethylene glycol or propylene glycol including, but not limited to, those available from BASF Corporation under the general trade 10 designation PLURONIC.

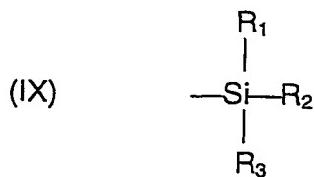
As indicated above, cationic surface active agents also can be used. Nonlimiting examples of cationic surface active agents suitable for use in the cured compositions or coatings of the present invention include acid salts of alkyl amines such as ARMAC HT, an acetic acid salt of n-alkyl amine available from 15 Akzo Nobel Chemicals; imidazoline derivatives such as CALGENE C-100 available from Calgene Chemicals Inc.; ethoxylated amines or amides such as DETHOX Amine C-5, a cocoamine ethoxylate available from Deforest Enterprises; ethoxylated fatty amines such as ETHOX TAM available from Ethox Chemicals, Inc.; and glyceryl esters such as LEXEMUL AR, a glyceryl stearate/stearaidoethyl 20 diethylamine available from Inolex Chemical Co.

Other examples of suitable surface active agents can include polyacrylates. Nonlimiting examples of suitable polyacrylates include homopolymers and copolymers of acrylate monomers, for example polybutylacrylate and copolymers derived from acrylate monomers (such as ethyl (meth)acrylate, 2- 25 ethylhexylacrylate, butyl (meth)acrylate and isobutyl acrylate), and hydroxy ethyl(meth)acrylate and (meth)acrylic acid monomers. In one embodiment, the polyacrylate can have amino and hydroxy functionality. Suitable amino and hydroxyl functional acrylates are disclosed in Example 26 below and in U.S. Patent No. 6,013,733, which is incorporated herein by reference. Another 30 example of a useful amino and hydroxyl functional copolymer is a copolymer of hydroxy ethyl acrylate, 2-ethylhexylacrylate, isobutyl acrylate and dimethylamino

ethylmethacrylate. In another embodiment, the polyacrylate can have acid functionality, which can be provided, for example, by including acid functional monomers such as (meth)acrylic acid in the components used to prepare the polyacrylate. In another embodiment, the polyacrylate can have acid functionality and hydroxyl functionality, which can be provided, for example, by including acid functional monomers such as (meth)acrylic acid and hydroxyl functional monomers such as hydroxy ethyl (meth)acrylate in the components used to prepare the polyacrylate.

In an alternative embodiment, the reactant can comprise at least one material which has at least one reactive functional group which is reversibly blocked with a silyl group. This silyl-blocked material is different from the first material, second material, dual cure material (if present) and curing agent of the composition. Hydrolysis of the silyl group regenerates the reactive functional group on the material which is available for further reaction with the curing agent.

Suitable silyl blocking groups can have the following structure (IX):



wherein each R_1 , R_2 and R_3 , which may be identical or different, represents an alkyl group having from 1 to 18 carbon atoms, a phenyl group or an allyl group.

Non-limiting examples of suitable functional groups which can be blocked by the silyl group comprise hydroxyl groups, carbamate groups, carboxyl groups, amide groups and mixtures thereof. In one embodiment, the functional groups are hydroxyl groups.

Non-limiting examples of suitable compounds which can be reacted with the functional group to form the silyl group comprise hexamethyldisilazane, trimethylchlorosilane, trimethylsilyldiethylamine, t-butyl dimethylsilyl chloride, diphenyl methylsilyl chloride, hexamethyl disilylazide, hexamethyl disiloxane, trimethylsilyl triflate, hexamethyldisilyl acetamide, N,N'-bis(trimethylsilyl)-urea and mixtures of any of the foregoing.

Further examples of suitable compounds for silylation reactions, and suitable reaction conditions and reagents for trimethylsilylation reactions are discussed in T. Greene et al., Protective Groups in Organic Synthesis, (2d. ed. 1991) at pages 68-86 and 261-263, which are incorporated herein by reference.

- 5 The backbone of the material can be a compound which comprises at least one linkage selected from an ester linkage, a urethane linkage, a urea linkage, an amide linkage, a siloxane linkage, and an ether linkage or a polymer such as a polyester, an acrylic polymer, a polyurethane, a polyether, a polyurea, a polyamide and copolymers of any of the foregoing.
- 10 Suitable compounds or polymers having ester groups and at least one reactive functional group include half-esters formed from reacting at least one polyol with at least one 1,2-anhydride. The half-esters are preferred because they are of relatively low molecular weight and are quite reactive with epoxy functionality.
- 15 The half-ester is obtained by reaction between a polyol and a 1,2-anhydride under conditions sufficient to ring open the anhydride forming the half-ester with substantially no polyesterification occurring. Such reaction products are of relatively low molecular weight with narrow molecular weight distributions and low viscosity. By "substantially no polyesterification occurring" means that the
- 20 carboxyl groups formed by the reaction of the anhydride are not further esterified by the polyol in a recurring manner. By this is meant that less than 10, or less than 5 percent by weight of high molecular weight polyester is formed.

- The 1,2-anhydride and polyol generally are mixed together and the reaction is conducted in the presence of an inert atmosphere such as nitrogen and a
- 25 solvent such as a ketone or aromatic hydrocarbon to dissolve the solid ingredients and/or lower the viscosity of the reaction mixture.

- For the desired ring opening reaction and half-ester formation, a 1,2-dicarboxylic anhydride is used. Reaction of a polyol with a carboxylic acid instead of an anhydride would require esterification by condensation and elimination water
- 30 would have to be removed by distillation. Under these conditions, this would promote undesired polyesterification. Also, the reaction temperature can be low,

i.e., less than 135°C or from 70°C to 135°C. The time of reaction can vary somewhat depending upon the temperature of reaction, and generally ranges from 10 minutes to 24 hours.

- The equivalent ratio of anhydride to hydroxyl on the polyol can be at least 5 0.8:1 (the anhydride being considered monofunctional) to obtain maximum conversion to the desired half-ester. Ratios less than 0.8:1 can be used but such ratios result in increased formation of lower functionality half-esters.

- Useful anhydrides include aliphatic, cycloaliphatic, olefinic, cycloolefinic and aromatic anhydrides. Substituted aliphatic and aromatic anhydrides also are 10 useful provided the substituents do not adversely affect the reactivity of the anhydride or the properties of the resultant polyester. Examples of substituents include chloro, alkyl and alkoxy. Examples of anhydrides include succinic anhydride, methylsuccinic anhydride, dodecanyl succinic anhydride, octadecenylsuccinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, 15 methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, alkyl hexahydrophthalic anhydrides such as methylhexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylene tetrahydrophthalic anhydride, chlorendio anhydride, itaconic anhydride, citraconic anhydride and maleic anhydride.
- 20 Among the polyols which can be used are simple polyols, that is, those containing from 2 to 20 carbon atoms, as well as polymeric polyols such as polyester polyols, polyurethane polyols and acrylic polyols.
- Among the simple polyols are diols, triols, tetrols and mixtures thereof. Non-limiting examples of the polyols include those containing from 2 to 10 carbon 25 atoms such as aliphatic polyols. Specific examples include but are not limited to the following compositions: di-trimethylol propane (bis(2,2-dimethylol)dibutylether); pentaerythritol; 1,2,3,4-butanetetrol; sorbitol; trimethylolpropane; trimethylolethane; 1,2,6-hexanetriol; glycerine; trishydroxyethyl isocyanurate; dimethylol propionic acid; 1,2,4-butanetriol; TMP/epsilon-caprolactone triols;
- 30 ethylene glycol; 1,2-propanediol; 1,3-propanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2-ethyl-1,3-hexanediol, neopentyl glycol; diethylene glycol;

dipropylene glycol; 1,4-cyclohexanedimethanol and 2,2,4-trimethylpentane-1,3 diol. In one embodiment, the polyol is trimethylolpropane.

With regard to oligomeric polyols, suitable polyols are polyols made from reaction of diacids with triols, such as trimethylol propane/cyclohexane diacid and 5 trimethylol propane/adipic acid.

With regard to polymeric polyols, the polyester polyols are prepared by esterification of an organic polycarboxylic acid or anhydride thereof with organic polyols and/or an epoxide. Usually, the polycarboxylic acids and polyols are aliphatic or aromatic dibasic acids or acid anhydrides and diols.

10 The polyols which are usually employed in making the polyester include trimethylol propane, di-trimethylol propane, alkylene glycols such as ethylene glycol, neopentyl glycol and other glycols such as hydrogenated bisphenol A, cyclohexanediol, cyclohexanedimethanol, the reaction products of lactones and diols, for example, the reaction product of epsilon-caprolactone and ethylene 15 glycol, hydroxy-alkylated bisphenols, polyester glycols, for example, poly(oxytetramethylene)glycol and the like.

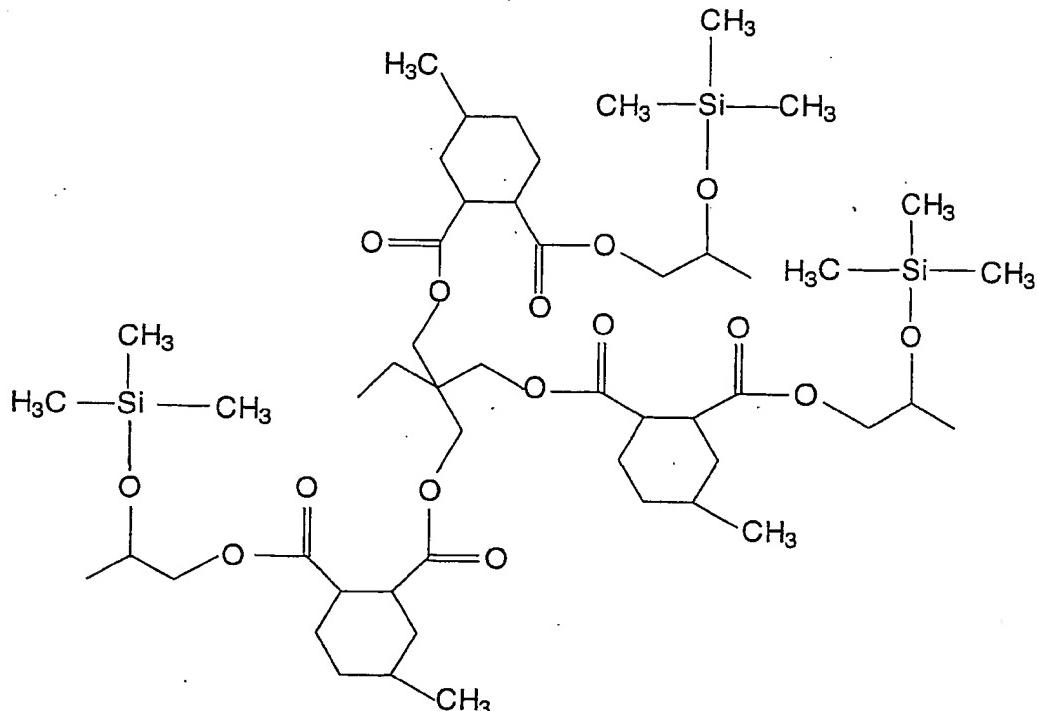
The acid component of the polyester consists primarily of monomeric carboxylic acids or anhydrides having 2 to 18 carbon atoms per molecule. Among the acids which are useful are phthalic acid, isophthalic acid, 20 terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, methylhexahydrophthalic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, chlorendic acid, tetrachlorophthalic acid and other dicarboxylic acids of varying types. Also, there may be employed higher polycarboxylic acids such as trimellitic acid and tricarballylic acid. However, the use of these higher 25 functionality polycarboxylic acids are not preferred because of resultant high viscosities.

Besides the polyester polyols formed from polybasic acids and polyols, polylactone-type polyesters also can be employed. These products are formed from the reaction of a lactone such as epsilon-caprolactone and a polyol such as 30 ethylene glycol, diethylene glycol and trimethylolpropane.

- Besides polyester polyols, polyurethane polyols such as polyester-urethane polyols which are formed from reacting an organic polyisocyanate with a polyester polyol such as those described above can be used. The organic polyisocyanate is reacted with a polyol so that the OH/NCO equivalent ratio is greater than 1:1 so
- 5 that the resultant product contains free hydroxyl groups. The organic polyisocyanate which is used in preparing the polyurethane polyols can be an aliphatic or aromatic polyisocyanate or a mixture. Diisocyanates may be used, although higher polyisocyanates such as triisocyanates also can be used, but these may result in higher viscosities.
- 10 Examples of suitable diisocyanates are 4,4'-diphenylmethane diisocyanate, 1,4-tetramethylene diisocyanate, isophorone diisocyanate and 4,4'-methylenebis(cyclohexyl isocyanate). Examples of suitable higher functionality polyisocyanates are polymethylene polyphenol isocyanates.
- At least a portion or all of the acid functional groups can be silylated.
- 15 Alternatively at least a portion or all of the acid functional groups can be converted to hydroxyl groups by reaction with an epoxy functional material such as are discussed above or aliphatic diol to provide alcoholic hydroxyl groups for silylation.
- Useful epoxy functional materials include epoxy functional monomers such as glycidyl methacrylate, ethylene oxide, butylene oxide, propylene oxide,
- 20 cyclohexene oxide, glycidyl ethers such as phenyl glycidyl ether, n-butyl glycidyl ether, cresyl glycidyl ether, and isopropyl glycidyl ether, glycidyl esters such as glycidyl versatate, for example CARDURA E available from Shell Chemical Co., and mixtures of any of the foregoing. The equivalent ratio of epoxy groups to acid groups on the ester generally ranges from 0.1:1 to 2:1, can range from 0.5:1 to
- 25 1:1, and typically ranges from 0.8:1 to 1:1.
- Useful aliphatic diols include diols containing a primary hydroxyl such as 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,2-pentanediol, 1,4-pentanediol, 1,2-hexanediol, 1,5-hexanediol, 2-ethyl-1,3-hexanediol, diethylene glycol, dipropylene glycol, 1,4-cyclohexanedimethanol,
- 30 2,2,4-trimethyl-1,3-pentanediol, and 3,3-dimethyl-1,2-butanediol.
- A non-limiting example of a silylated compound containing ester groups for

use in the coating compositions of the present invention has the following structure (X):

(X)



5

Other useful materials having ester, urethane, urea, amide and/or ether groups and at least one reactive functional group which are suitable for silylation are disclosed above in the discussion of suitable additional polymers.

- 10 Alternatively, useful reactants include acrylic polymers containing hydroxyl groups blocked with hydrolyzable siloxy groups (polymerized for example from vinyl monomers and trimethyl siloxy methylmethacrylate) such as are disclosed in I. Azuma et al., "Acrylic Oligomer for High Solid Automotive Top Coating System Having Excellent Acid Resistance", *Progress in Organic Coatings* 32 (1997) 1-7, 15 which is incorporated herein by reference.

In one embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the composition, is present in the composition in an

amount ranging from 0.1 to 90 weight percent based on total weight of the resin solids of the components which form the composition. In another embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount of at least 0.1 weight percent based on total weight of the resin solids of the components which form the coating composition. In another embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount of at least 1 weight percent based on total weight of the resin solids of the components which form the coating composition. In another embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount of at least 5 weight percent based on total weight of the resin solids of the components which form the coating composition.

In yet another embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount less than 60 weight percent based on total weight of the resin solids of the components which form the coating composition. In a further embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount less than 30 weight percent based on total weight of the resin solids of the components which form the coating composition. In another embodiment, the present invention is directed to compositions as previously described wherein the silyl-blocked reactant, when added to the other components which form the coating composition, is present in the coating composition in an amount less than 10 weight percent based on total weight of the resin solids of the components which form the coating composition. The amount

of the silyl-blocked reactant may range between any combination of these values inclusive of the recited values.

The coating compositions of the present invention can be solvent-based coating compositions, water-based coating compositions, in solid particulate form, 5 that is, a powder coating composition, or in the form of a powder slurry or aqueous dispersion. The components of the present invention used to form the cured compositions of the present invention can be dissolved or dispersed in an organic solvent. Nonlimiting examples of suitable organic solvents include alcohols, such as butanol; ketones, such as methyl amyl ketone; aromatic hydrocarbons, such as 10 xylene; and glycol ethers, such as, ethylene glycol monobutyl ether; esters; other solvents; and mixtures of any of the foregoing.

In solvent based compositions, the organic solvent is generally present in amounts ranging from 5 to 80 percent by weight based on total weight of the resin solids of the components which form the composition, and can be present in an 15 amount ranging from 30 to 50 percent by weight, inclusive of the recited values. The compositions as described above can have a total solids content ranging from 40 to 75 percent by weight based on total weight of the resin solids of the components which form the composition, and can have a total solids content ranging from 50 to 70 percent by weight, inclusive of the recited values. 20 Alternatively, the inventive compositions can be in solid particulate form suitable for use as a powder coating, or suitable for dispersion in a liquid medium such as water for use as a powder slurry.

In a further embodiment, a catalyst can be present during the coating composition's formation. Nonlimiting examples of suitable catalysts include acidic 25 materials, for example acid phosphates, such as phenyl acid phosphate, and substituted or unsubstituted sulfonic acids such as dodecylbenzene sulfonic acid or para-toluene sulfonic acid and other catalysts such as N,N'-dimethyldodecyl amine catalysts and tin catalysts such as dibutyl tin dilaurate. The catalyst can be present, when added to the other components which form the coating 30 composition, in an amount ranging from 0.1 to 5.0 percent by weight based on the

total weight of the resin solids of the components which form the coating composition, inclusive of the recited values.

- In another embodiment, additional components can be present during the formation of the coating compositions as previously described. These additional components include, but are not limited to, flexibilizers, plasticizers, surface active agents as defined herein (such as, for example polysiloxanes), thixotropic agents, anti-gassing agents, organic cosolvents, flow controllers, hindered amine light stabilizers, anti-oxidants, UV light absorbers, coloring agents or tints, and similar additives conventional in the art, as well as mixtures of any of the foregoing can be included in the coating composition. These additional ingredients can present, when added to the other components which form the coating composition, in an amount up to 40 percent by weight based on the total weight of the resin solids of the components which form the coating composition, inclusive of the recited values.
- The amount of the coating composition applied to the substrate can vary based upon such factors as the type of substrate and intended use of the substrate, i.e., the environment in which the substrate is to be placed and the nature of the contacting materials.
- In yet another embodiment, the present invention is directed to a coated substrate comprising a substrate and a coating composition coated over at least a portion of the substrate, wherein the coating composition is selected from any of the foregoing coating compositions. In still another embodiment, the present is directed to a method of coating a substrate which comprises applying a coating composition over at least a portion of the substrate, wherein the coating composition is selected from any of the foregoing coating compositions.

- In another embodiment, the present invention is directed to a method of coating a substrate further comprising a step of curing the coating composition after application to the substrate. The components used to form the coating compositions in these embodiments can be selected from the components discussed above, and additional components also can be selected from those recited above.

As used herein, a composition "over at least a portion of a substrate" refers to a composition directly applied to at least a portion of the substrate, as well as a composition applied to any coating material which was previously applied to at least a portion of the substrate.

- 5 The coating compositions of the present invention can be applied over virtually any substrate including wood, metals, glass, cloth, plastic, foam, polymeric substrates such as elastomeric substrates, and the like. In one embodiment, the present invention is directed to a coated substrate as previously described wherein the coated substrate is a flexible substrate. In another
- 10 embodiment, the present invention is directed to a coated substrate as previously described wherein the coated substrate is a rigid substrate.

- In a further embodiment, the present invention is directed to coated substrates as previously described wherein the coated substrate is a ceramic substrate. In still another embodiment, the present invention is directed to coated substrates as previously described wherein the coated substrate is a polymeric substrate. In another embodiment, the present invention is directed to a coated metallic substrate comprising a metallic substrate and a cured composition coated over at least a portion of the metallic substrate, wherein the cured composition is selected from any of the foregoing compositions. The components used to form the cured compositions in these embodiments can be selected from the components discussed above, and additional components also can be selected from those recited above.
- 15
 - 20

- A further embodiment of the present invention is directed to a coated automobile substrate comprising an automobile substrate and a cured composition coated over at least a portion of the automobile substrate, wherein the cured composition is selected from any of the foregoing compositions. In yet another embodiment, the present invention is directed to a method of making a coated automobile substrate comprising providing an automobile substrate and applying over at least a portion of the automotive substrate a coating composition selected from any of the foregoing compositions. Again, the components used to form the cured compositions in these embodiments can be selected from the
- 25
 - 30

components discussed above, and additional components also can be selected from those recited above.

Suitable flexible elastomeric substrates can include any of the thermoplastic or thermoset synthetic materials well known in the art. Nonlimiting examples of suitable flexible elastomeric substrate materials include polyethylene, polypropylene, thermoplastic polyolefin ("TPO"), reaction injected molded polyurethane ("RIM"), and thermoplastic polyurethane ("TPU").

Nonlimiting examples of thermoset materials useful as substrates in connection with the present invention include polyesters, epoxides, phenolics, polyurethanes such as "RIM" thermoset materials, and mixtures of any of the foregoing. Nonlimiting examples of suitable thermoplastic materials include thermoplastic polyolefins such as polyethylene, polypropylene, polyamides such as nylon, thermoplastic polyurethanes, thermoplastic polyesters, acrylic polymers, vinyl polymers, polycarbonates, acrylonitrile-butadiene-styrene ("ABS") copolymers, ethylene propylene diene terpolymer ("EPDM") rubber, copolymers, and mixtures of any of the foregoing.

Nonlimiting examples of suitable metal substrates include ferrous metals (e.g., iron, steel, and alloys thereof), nonferrous metals (e.g., aluminum, zinc, magnesium, and alloys thereof), and mixtures of any of the foregoing. In the particular use of automobile components, the substrate can be formed from cold rolled steel, electrogalvanized steel such as hot dip electrogalvanized steel, electrogalvanized iron-zinc steel, aluminum, and magnesium.

When the substrates are used as components to fabricate automotive vehicles (including, but not limited to, automobiles, trucks and tractors) they can have any shape, and can be selected from the metallic and flexible substrates described above. Typical shapes of automotive body components can include bodies (frames), hoods, doors, fenders, bumpers, and trim for automotive vehicles.

In a further embodiment, the present invention is directed to coated automotive substrates as previously described wherein the coated automotive substrate is a hood. In another embodiment, the present invention is directed to

coated automotive substrates as previously described wherein the coated automotive substrate is a door. In another embodiment, the present invention is directed to coated automotive substrates as previously described wherein the coated automotive substrate is a fender. In another embodiment, the present

5 invention is directed to coated automotive substrates as previously described wherein the coated automotive substrate is a quarterpanel. The components used to form the cured compositions used to coat the automotive substrates in these embodiments can be selected from the components discussed above.

In embodiments of the present invention directed to automotive

10 applications, the cured compositions can be, for example, the electrodeposition coating, the primer coating, the basecoat, and/or the topcoat. Suitable topcoats include monocoats and basecoat/clearcoat composites. Monocoats are formed from one or more layers of a colored coating composition. Basecoat/clearcoat composites comprise one or more layers of a colored basecoat composition, and

15 one or more layers of a clearcoating composition, wherein the basecoat composition has at least one component which is different from the clearcoat composition. In the embodiments of the present invention directed to automotive applications, the clearcoat can be transparent after application.

In another embodiment, the present invention is directed to multi-

20 component composite cured compositions comprising a basecoat deposited from a pigmented coating composition, and a topcoating composition applied over the basecoat, wherein the topcoating composition is selected from any of the compositions previously described.

In one embodiment, the present invention is directed to a multi-component

25 composite cured composition as previously described, wherein the topcoating composition is transparent after curing and is selected from any of the cured compositions previously described. The components used to form the topcoating composition in these embodiments can be selected from the coating components discussed above, and additional components also can be selected from those

30 recited above.

The basecoat and transparent topcoat (i.e., clearcoat) compositions used in

the multi-component composite cured compositions of the present invention in certain instances can be formulated into liquid high solids compositions, that is, compositions containing 40 percent, or greater than 50 percent by weight resin solids. The solids content can be determined by heating a sample of the cured composition to 105°C to 110°C for 1-2 hours to drive off the volatile material, and subsequently measuring relative weight loss. As aforementioned, although the cured compositions can be formed from liquid coating compositions, they also can be formed from coating compositions formulated as powder coating compositions.

The coating composition of the basecoat in the color-plus-clear system can 10 be any of the compositions useful in coatings applications, particularly automotive applications. The coating composition of the basecoat can be formed from components comprising a resinous binder and a pigment to act as the colorant. Nonlimiting examples of resinous binders are acrylic polymers, polyesters, alkyds, and polyurethanes.

15 The resinous binders for the basecoat can be organic solvent-based materials such as those described in U.S. Patent No. 4,220,679, note column 2, line 24 continuing through column 4, line 40, which portions is incorporated by reference. Also, water-based coating compositions such as those described in U.S. Patent Nos. 4,403,003, 4,147,679 and 5,071,904 can be used as the binder 20 in the basecoat composition. These U.S. patents are incorporated herein by reference.

The basecoat composition can comprise one or more pigments as colorants. Nonlimiting examples of suitable metallic pigments include aluminum flake, copper bronze flake, and metal oxide coated mica.

25 Besides the metallic pigments, the basecoat compositions can contain nonmetallic color pigments conventionally used in surface coatings such as, for example inorganic pigments such as titanium dioxide, iron oxide, chromium oxide, lead chromate, and carbon black; and organic pigments such as phthalocyanine blue and phthalocyanine green.

30 Optional ingredients in the basecoat composition can comprise those which are well known in the art of formulating surface coatings and can comprise

surface active agents, flow control agents, thixotropic agents, fillers, anti-gassing agents, organic co-solvents, catalysts, and other customary auxiliaries.

Nonlimiting examples of these materials and suitable amounts are described in U.S. Patent Nos. 4,220,679; 4,403,003; 4,147,769; and 5,071,904, which are

- 5 incorporated herein by reference.

The basecoat compositions can be applied to the substrate by any conventional coating technique such as brushing, spraying, dipping, or flowing. Spray techniques and equipment for air spraying, airless spray, and electrostatic spraying in either manual or automatic methods, known in the art can be used.

- 10 During application of the basecoat to the substrate, the film thickness of the basecoat formed on the substrate can range from 0.1 to 5 mils. In another embodiment, the film thickness of the basecoat formed on the substrate can range 0.1 to 1 mils, and can be 0.4 mils.

- 15 After forming a film of the basecoat on the substrate, the basecoat can be cured or alternatively given a drying step in which solvent is driven out of the basecoat film by heating or an air drying period before application of the clearcoat. Suitable drying conditions may depend on the particular basecoat composition, and on the ambient humidity if the composition is water-borne, but a drying time from 1 to 15 minutes at a temperature of 75° to 200°F can be adequate.

- 20 The transparent or clear topcoat composition can be applied to the basecoat by any conventional coating technique, including, but not limited to, compressed air spraying, electrostatic spraying, and either manual or automatic methods. The transparent topcoat can be applied to a cured or to a dried basecoat before the basecoat has been cured. In the latter instance, the two
- 25 coatings can then be heated to cure both coating layers simultaneously. The clearcoating thickness (dry film thickness) can be 1 to 6 mils.

The coating composition can be cured by the combination of ionizing or actinic radiation and thermal energy as described in detail above. Typical radiation energy curing conditions are discussed in detail above. Typical thermal energy curing conditions can range from 50°F to 475°F (10°C to 246°F) for 1 to 30 minutes.

A second topcoat coating composition can be applied to the first topcoat to form a "clear-on-clear" topcoat. The first topcoat coating composition can be applied over the basecoat as described above. The second topcoat coating composition can be applied to a cured or to a dried first topcoat before the 10 basecoat and first topcoat have been cured. The basecoat, the first topcoat, and the second topcoat can then be heated to cure the three coatings simultaneously.

It should be understood that the second transparent topcoat and the first transparent topcoat coating compositions can be the same or different provided that, when applied wet-on-wet, one topcoat does not substantially interfere with 15 the curing of the other for example by inhibiting solvent/water evaporation from a lower layer. Moreover, the first topcoat, the second topcoat or both can be the cured composition of the present invention. The first transparent topcoat composition can be virtually any transparent topcoating composition known to those skilled in the art. The first transparent topcoat composition can be water- 20 borne or solventborne, or, alternatively, in solid particulate form, i.e., a powder coating.

Nonlimiting examples of suitable first topcoating compositions include crosslinkable coating compositions comprising at least one thermosettable coating material and at least one curing agent. Suitable waterborne clearcoats are 25 disclosed in U.S. Patent No. 5,098,947, which patent is incorporated herein by reference, and are based on water-soluble acrylic resins. Useful solvent borne clearcoats are disclosed in U.S. Patent Nos. 5,196,485 and 5,814,410, which patents are incorporated herein by reference, and include polyepoxides and polyacid curing agents. Suitable powder clearcoats are described in U.S. Patent 30 No. 5,663,240, which is incorporated herein by reference, and include epoxy functional acrylic copolymers and polycarboxylic acid curing agents.

Typically, after forming the first topcoat over the basecoat, the first topcoat is given a drying step in which solvent is driven out of the film by heating or, alternatively, an air drying period or curing step, before the application of the second topcoat. Suitable drying conditions will depend on the particular first 5 topcoat composition, and on the ambient humidity if the composition is water-borne, but, in general, a drying time from 1 to 15 minutes at a temperature of 75° to 200°F will be adequate.

The polysiloxane-containing second topcoat coating composition of the present invention can be applied as described above for the first topcoat by any 10 conventional coating application technique. Curing conditions can be those described above for the topcoat. The second topcoating dry film thickness can range from 0.1 to 3 mils (7.5 micrometers to 75 micrometers).

It should be mentioned that the polysiloxane-containing coating compositions can be advantageously formulated as a "monocoat," that is a 15 coating which forms essentially one coating layer when applied to a substrate. The monocoat coating composition can be pigmented. Nonlimiting examples of suitable pigments include those mentioned above. When employed as a monocoat, the polysiloxane-containing coating compositions of the present invention can be applied (by any of the conventional application techniques 20 discussed above) in two or more successive coats, and, in certain instances can be applied with only an ambient flash period between coats. The multi-coats when cured can form essentially one coating layer.

In another embodiment, the present invention is directed to a method for making a multi-component composite comprising (a) applying a pigmented 25 composition to a substrate to form a basecoat; and (b) applying a topcoating composition over at least a portion of the basecoat to form a topcoat thereon, wherein the topcoating composition is selected from any of the compositions described above. The components used to form the topcoating composition in this embodiment can be selected from the coating components discussed above, and 30 additional components also can be selected from those recited above.

The coatings formed from the cured compositions according to the present invention can have outstanding appearance properties and initial scratch (mar) resistance properties, as well as post-weathering or "retained" scratch (mar) resistance, which can be evaluated by measuring the gloss of coated substrates
5 before and after abrading of the coated substrates.

The initial 20° gloss of a coated substrate according to the present invention can be measured with a 20° NOVO-GLOSS 20 statistical glossmeter, available from Gardner Instrument Company, Inc. The coated substrate can be subjected to scratch testing by linearly scratching the coating or substrate with a
10 weighted abrasive paper for ten double rubs using an Atlas AATCC Scratch Tester, Model CM-5, available from Atlas Electrical Devices Company of Chicago, Illinois. The abrasive paper is 3M 281Q WETORDRY™ PRODUCTION™ 9 micron polishing paper sheets, which are commercially available from 3M Company of St. Paul, Minnesota. Panels are then rinsed with tap water and
15 carefully patted dry with a paper towel. The 20° gloss is measured on the scratched area of each test panel. The number reported is the percent of the initial gloss retained after scratch testing, i.e., 100% X scratched gloss / initial gloss. This test method is fully disclosed in the examples that follow.

In one embodiment, the present invention is directed to cured compositions
20 having an initial 20° gloss (as measured using a 20° NOVO-GLOSS 20 statistical glossmeter, available from Gardner Instrument Company described above) of greater than 40, the compositions being any of the foregoing compositions according to the present invention. In another embodiment, the present invention is directed to cured compositions having an initial 20° gloss (as measured using a
25 20° NOVO-GLOSS 20 statistical glossmeter, available from Gardner Instrument Company described above) of greater than 50, or greater than 70, the compositions being any of the foregoing compositions according to the present invention.

Moreover, in another embodiment, the present invention is directed to
30 cured compositions having a post-weathering or "retained" scratch resistance value such that after scratch testing, greater than 40 percent of initial 20° gloss is

retained. Moreover, the cured compositions of the present invention can have a post-weathering scratch resistance (as measured using the scratch test method described above after the unscratched test panels were subjected to simulated weathering by QUV exposure to UVA-340 bulbs in a weathering cabinet available from Q Panel Company) such that greater than 50 percent, or greater than 60 percent of initial 20° gloss is retained after weathering.

In one embodiment, the present invention is directed to methods of improving the scratch resistance of a substrate comprising applying to the substrate any of the inventive compositions described for the substrate. In another embodiment, the present invention is directed to a method of improving the dirt repellency of a substrate comprising applying to the substrate any of the inventive compositions described for the substrate.

In another embodiment, the present invention is directed to a method for retaining the gloss of a substrate over time comprising applying to the substrate comprising any of the inventive compositions described for the substrate. In another embodiment, the present invention is directed to a method for revitalizing the gloss of a substrate comprising applying to the substrate any of the inventive compositions described for the substrate.

In another embodiment, the cured compositions of the present invention also can be useful as decorative or protective coatings for pigmented plastic (elastomeric) substrates, such as those described above, or mold-in-color ("MIC") plastic substrates. In these applications, the compositions can be applied directly to the plastic substrate or included in the molding matrix. Optionally, an adhesion promoter can first be applied directly to the plastic or elastomeric substrate and the composition applied as a topcoat thereover. The compositions of the present invention also can be advantageously formulated as pigmented coating compositions for use as primer coatings, as basecoats in multi-component composite coatings, and as monocoat topcoats including pigments or colorants. The components used to form the compositions in these embodiments can be selected from the coating components discussed above, and additional components also can be selected from those recited above.

- In yet another embodiment of the present invention, a cured composition is provided which comprises particles dispersed in a cured composition comprising one or more thermoplastic materials. As previously described, the concentration of particles is greater in the surface region than in the bulk region. The cured
- 5 composition can be derived from a thermoplastic resinous coating composition. Nonlimiting examples of suitable thermoplastic materials include high molecular weight (i.e., Mw greater than 20,000, greater than 40,000, or greater than 60,000), acrylic polymers, polyolefin polymers, polyamide polymers, and polyester polymers suitable for use in lacquer dry systems. One nonlimiting example of a
- 10 class of thermoplastic materials from which the cured composition can be derived is fluoropolymer-acrylic copolymers such as those prepared from polyvinylidene fluoride, for example KYNAR 500 (available from Ausimont USA, Inc.) and thermoplastic acrylic copolymers, such as ACRYLOID B44 (65% methyl methacrylate and 35% ethyl acrylate), available from Dock Resin, Inc.
- 15 In another embodiment, the present invention is directed to a method for retaining the gloss of a polymeric substrate or polymer coated substrate after a predetermined period of time comprising applying to the substrate comprising any of the inventive compositions described for the substrate. This predetermined period of time can generally be at least 6 months and can be at least one year. In
- 20 another embodiment, the present invention is directed to a method for revitalizing the gloss of a polymeric substrate or polymer coated substrate comprising applying to the substrate any of the inventive compositions described above.

Illustrating the invention is the following example which, however, is not to be considered as limiting the invention to their details. Unless otherwise indicated, all parts and percentages in the following examples, as well as throughout the specification, are by weight.

EXAMPLE

A dual cure (ultraviolet radiation and thermal cure) coating composition was

30 prepared and evaluated as discussed below.

The coating composition was made by adding each of the ingredients under agitation in the order listed in Table 1 below. The acrylic polyol and isocyanurate were preblended before the addition to the other ingredients.

5

Table 1

Ingredient	Description	<u>Solids</u>	Weight
SR355 ¹	DiTMP Tetraacrylate	27.3	27.3
Clariant HIGHLINK OG 108-32	Colloidal Silica in tripropylene glycol diacrylate	41.9	41.9
DAROCURE 4265 ³	Photoinitiator	2.0	2.0
TINUVIN 400 ³	UV Absorber	3.0	3.0
TINUVIN 292 ³	Hindered Amine Light Stabilizer	0.8	0.8
RC-68-1497 ²	Acrylic Polyol Resin	15.6	23.3
DESMODUR N-3300 ⁴	Isocyanurate of HDI	9.4	9.4
	Total	100.0	107.7

¹ D trimethylolpropane tetraacrylate which is available from Sartomer Company, Inc.

² Acrylic polyol prepared from 14.5% butyl acrylate, 14.5% butyl methacrylate, 27.5% isobornyl methacrylate, 22.6% hydropropyl methacrylate, 20.4% hydroxyethyl methacrylate, 0.4% acrylic acid and having the following properties: Solids 67% in Aromatic 100 solvent, M_w 2336, M_n 1236 and OH Value of 116.8.

³ Phosphine Oxide as a 50:50 blend of 2-hydroxy-2-methyl-1-phenyl propan-1-one and 2,4,6-trimethyl benzoyl diphenyl phosphine oxide such as DAROCURE 4265, which is commercially available from Ciba-Geigy Corporation.

⁴ Isocyanurate of hexamethylene diisocyanate available from Bayer Corporation.

The coating composition was applied over pretreated and basecoated panels as described below. The panels used were cold rolled steel panels (size 4 inches x 12 inches (10.16 cm by 30.48 cm)) coated with ED5000 electrocoat (available from PPG Industries, Inc). The test panels are available from ACT Laboratories, Inc. of Hillsdale, Michigan. The basecoat (BWB-8555 black waterborne basecoat available from PPG Industries, Inc.) was spray applied at 0.6 mils (15 micrometers) dry film thickness and fully baked for 30 minutes at 285°F (141°C). The coating composition of the present invention was applied using a 7 mil (179 micrometers) drawdown bar over the basecoat to approximately 1.0-1.2 mils (26-31 micrometers) dry film thickness. The clearcoat was flashed at ambient temperature (25°C) for five minutes and then cured using ultraviolet light at 576

mJoules/cm² at a line speed of 70 feet per minute (21.3 meters per minute) and then thermally cured for 30 minutes at 285°F (141°C).

- The coating on the panel was evaluated for scratch resistance as follows.
- 20° gloss was measured with a Statistical Novo-Gloss 20° gloss meter, available
- 5 from Paul N. Gardner Company, Inc. Coated panels were subjected to scratch testing by linearly scratching the coated surface with a weighted abrasive paper for ten double rubs using an Atlas AATCC Scratch Tester, Model CM-5, available from Atlas Electrical Devices Company of Chicago, Illinois. The abrasive paper used was 3M 281Q WETORDRY™ PRODUCTION™ 9 micron polishing paper
- 10 sheets, which are commercially available from 3M Company of St. Paul, Minnesota. Panels were then rinsed with tap water and carefully patted dry with a paper towel. The 20° gloss was measured (using the same gloss meter as that used for the initial 20° gloss) on the scratched area of each test panel. Using the lowest 20° gloss reading from the scratched area, the scratch results are reported
- 15 as the percent of the initial gloss retained after scratch testing using the following calculation: 100% * scratched gloss ÷ initial gloss. Higher values for percent of gloss retained are desirable.

The test results are given in Table 2 below.

20

Table 2

Clearcoat	Initial 20° Gloss	20° Gloss after Scratch Testing	% Gloss Retention
UV / Thermal Dual Cure	82	79	96

- The compositions of the present invention can provide numerous advantages in coating applications, including, but not limited to, good initial and
- 25 retained scratch resistance, good appearance properties such as gloss and distinctiveness of image, and physical properties such as good flexibility and weatherability.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive

concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.

1. A coating composition formed from components comprising:
 - (a) at least one first material comprising at least one radiation curable reactive functional group;
 - (b) at least one second material comprising at least one thermally curable reactive functional group;
 - (c) at least one curing agent reactive with the at least one thermally curable reactive functional group, the at least one curing agent being selected from aminoplast resins, polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing; and
 - (d) a plurality of particles selected from inorganic particles, composite particles, and mixtures of the foregoing,
- 15 wherein each component is different.
2. A coating composition according to claim 1, wherein the at least one radiation curable reactive functional group is selected from vinyl groups, vinyl ether groups, unsaturated ester groups, epoxy groups, maleimide groups, and fumarate groups.
- 20
3. A coating composition according to claim 2, wherein the at least one radiation curable reactive functional group is an unsaturated ester group selected from acrylate groups, methacrylate groups, and ethacrylate groups.
- 25
4. A coating composition according to claim 3, wherein the unsaturated ester group is an acrylate group.
5. A coating composition according to claim 1, wherein the first material comprises polysiloxane.

6. A coating composition according to claim 1, wherein the first material, when added to other components that form the coating composition, is present in the coating composition in an amount ranging from 1 to 99 weight percent based on total weight of the resin solids of the components which form the
5 coating composition

7. A coating composition according to claim 1, wherein the at least one radiation curable reactive functional group is curable by ionizing radiation.

10 8. A coating composition according to claim 1, wherein the at least one radiation curable reactive functional group is curable by actinic radiation.

9. A coating composition according to claim 1, wherein the at least one radiation curable reactive functional group is curable by ultraviolet radiation.

15

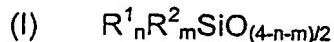
10. A coating composition according to claim 1, wherein the at least one thermally curable reactive functional group is selected from the group consisting of hydroxyl groups, vinyl groups, urethane groups, urea groups, amide groups, carbamate groups, isocyanate groups, blocked isocyanate groups, epoxy groups,
20 carbonyl groups, amine groups, anhydride groups, hydroxyalkyl amide groups, and aziridine groups.

11. A coating composition according to claim 1, wherein the second material is a film-forming polymer selected from the group consisting of hydroxyl
25 functional polymers, polyesters, acrylic polymers, polyurethanes, polyureas, polyamides, carbamate functional polymers, polyisocyanates different from curing agent (c), blocked polyisocyanates different from curing agent (c), polyepoxides different from curing agent (c), polyethers, polyacids different from curing agent (c), polyamines, polyanhydrides and copolymers and mixtures of the foregoing.

30

12. A coating composition according to claim 11, wherein the second material comprises at least one polysiloxane.

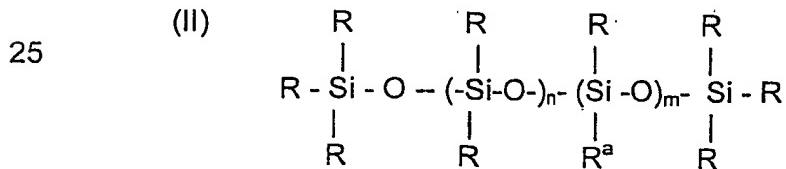
13. A coating composition according to claim 12, wherein the at least 5 one polysiloxane comprises at least one of the following structural units (I) :



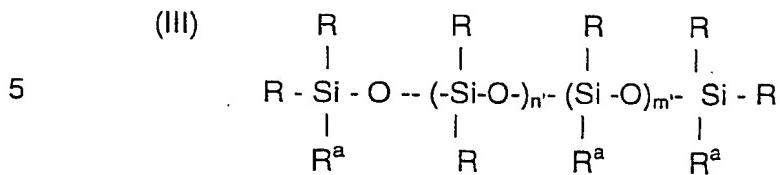
wherein each R^1 , which may be identical or different, represents H, OH, a monovalent hydrocarbon group or a monovalent siloxane group; each R^2 , which may be identical or different, represents a group comprising at least one reactive 10 functional group, wherein m and n each represents a number fulfilling the requirements of $0 < n < 4$, $0 < m < 4$ and $2 \leq (m+n) < 4$.

14. A coating composition according to claim 13, wherein each R^2 , which may be identical or different, represents a group comprising at least one 15 reactive functional group selected from a hydroxyl group, a carboxyl group, an isocyanate group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group, a maleimide group, a fumarate group, an anhydride group, a hydroxy alkylamide group, and an epoxy 20 group.

15. A composition according to claim 12, wherein the at least one polysiloxane has the following structure (II) or (III):



30 or



wherein:

- 10 m has a value of at least 1;
 - m' ranges from 0 to 75;
 - n ranges from 0 to 75;
 - n' ranges from 0 to 75;
 - each R, which may be identical or different, is selected from H, OH, monovalent hydrocarbon groups, monovalent siloxane groups, and mixtures of any of the foregoing; and
 - 15 -R^a comprises the following structure (IV):
- $$\begin{array}{c}
 \text{(IV)} \quad -\text{R}^3-\text{X}
 \end{array}$$
- wherein -R³ is selected from an alkylene group, an oxyalkylene group, an alkylene aryl group, an alkenylene group, an oxyalkenylene group, and an alkenylene aryl group; and
 - 20 X represents a group which comprises at least one reactive functional group selected from a hydroxyl group, a carboxyl group, an isocyanate group, a blocked polyisocyanate group, a primary amine group, a secondary amine group, an amide group, a carbamate group, a urea group, a urethane group, a vinyl group, an unsaturated ester group, a maleimide group, a fumarate group, an anhydride group, a hydroxy alkylamide group, and an epoxy group.

- 16. A coating composition according to claim 12, wherein the at least one polysiloxane is present in an amount of 0.5 to 75 weight percent on a basis of total weight of the resin solids of the components which form the coating composition.

17. A coating composition according to claim 1, wherein the second material, when added to other components that form the coating composition, is present in the coating composition in an amount ranging from 0.5 to 98.5 weight percent based on total weight of the resin solids of the components which form the
5 coating composition.

18. A coating composition according to claim 1, wherein the curing agent is selected from an aminoplast resin, a polyisocyanate and a blocked polyisocyanate.

10

19. A coating composition according to claim 18, wherein the curing agent is a polyisocyanate.

15

20. A coating composition according to claim 1, wherein the curing agent, when added to other components that form the coating composition, is present in the coating composition in an amount ranging from 0.5 to 65 weight percent based on total weight of the resin solids of the components which form the coating composition.

20

21. A coating composition according to claim 1, wherein the particles are selected from fumed silica, amorphous silica, colloidal silica, alumina, colloidal alumina, titanium dioxide, cesium oxide, yttrium oxide, colloidal yttria, zirconia, colloidal zirconia and mixtures of any of the foregoing.

25

22. A coating composition according to claim 1, wherein the particles are surface treated.

23. A coating composition according to claim 21, wherein the particles include colloidal silica.

30

24. A coating composition according to claim 1, wherein the particles have an average particle size of less than 100 micrometers prior to incorporation into the composition.

5 25. A coating composition according to claim 24, wherein the particles have an average particle size of less than 50 micrometers prior to incorporation into the composition.

10 26. A coating composition according to claim 1, wherein the particles have an average particle size ranging from 1 to less than 1000 nanometers prior to incorporation into the composition.

15 27. A coating composition according to claim 26, wherein the particles have an average particle size ranging from 1 to 100 nanometers prior to incorporation into the composition.

20 28. A coating composition according to claim 27, wherein the particles have an average particle size ranging from 5 to 50 nanometers prior to incorporation into the composition.

25 29. A coating composition according to claim 1, wherein the particles, when added to the other components that form the composition, are present in the composition in an amount ranging from 0.01 to 75 weight percent based on total weight of the resin solids of the components which form the composition.

30 30. A coating composition according to claim 29, wherein the particles are present in an amount of at least 0.1 weight percent.

30 31. A coating composition according to claim 30, wherein the particles are present in an amount of at least 0.5 weight percent.

32. A coating composition according to claim 31, wherein the particles are present in an amount of at least 5 weight percent.

5 33. A coating composition according to claim 1, wherein the components which form the composition comprise at least one surface active agent.

34. A coating composition according to claim 33, wherein the at least one surface active agent is selected from an anionic surface active agent, a
10 nonionic surface active agent and a cationic surface active agent.

35. A coating composition according to claim 1, wherein the components which form the composition comprise at least one photoinitiator.

15 36. A coating composition according to claim 35, wherein the at least one photoinitiator is selected from benzoin, benzophenone, hydroxy benzophenone, anthraquinone, thioxanthone, substituted benzoins such as butyl isomers of benzoin ethers, α,α -diethoxyacetophenone, α,α -dimethoxy- α -phenylacetophenone, 2-hydroxy-2-methyl-1-phenyl propane 1-one, 2,4,6-trimethyl 20 benzoyl diphenyl phosphine oxide, and mixtures of the foregoing.

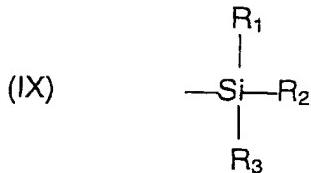
37. A coating composition according to claim 35, wherein the at least one photoinitiator is a 50:50 blend of 2-hydroxy-2-methyl-1-phenyl propan-1-one and 2,4,6-trimethyl benzoyl diphenyl phosphine oxide.

25

38. A coating composition according to claim 1, wherein the components from which the composition is formed comprise at least one material which has at least one reactive functional group which is blocked with a silyl group.

30 39. A coating composition according to claim 38, wherein the silyl blocking group has the following structure (IX):

5



wherein each R_1 , R_2 and R_3 , which may be identical or different, represents an alkyl group having from 1 to 18 carbon atoms, a phenyl group or an allyl group.

10

40. A coating composition according to claim 1, wherein the composition when cured has an initial scratch resistance value such that after scratch testing greater than 40 percent of the initial 20° gloss is retained.

15

41. A coating composition according to claim 1, wherein the composition when cured has a retained scratch resistance value such that after scratch testing greater than 30 percent of the initial 20° gloss is retained.

20

42. A cured coating formed from the composition of claim 1.

43. A cured composition according to claim 42, wherein the cured composition is cured by exposure to (1) ionizing radiation or actinic radiation and (2) thermal energy.

25

44. A cured composition according to claim 42, wherein the cured composition is cured by exposure to (1) ultraviolet radiation and (2) thermal energy.

30

45. A coated substrate comprising a substrate and a composition according to claim 1 deposited over at least a portion of the substrate.

46. A method for forming a cured coating on a substrate comprising applying over at least a portion of the substrate a coating composition according to claim 1.

5 47. A method according to claim 46, comprising the step of exposing the coating composition to (1) ionizing radiation or actinic radiation and (2) thermal energy.

10 48. A method according to claim 46, wherein the substrate is an automotive substrate.

49. A coated automobile substrate comprising an automobile substrate and a composition according to claim 1 deposited over at least a portion of the automobile substrate.

15

50. A coated automobile substrate according to claim 49, wherein the automobile substrate is a bumper.

20 51. A coated automobile substrate according to claim 49, wherein the automobile substrate is a hood.

52. A coated automobile substrate according to claim 49, wherein the automobile substrate is a door.

25 53. A coated automobile substrate according to claim 49, wherein the automobile substrate is a fender.

30 54. A multi-component composite coating composition comprising a basecoat deposited from a pigmented coating composition, and a composition according to claim 1 applied over at least a portion of the basecoat.

55. A multi-component composite according to claim 54, wherein the composition is a topcoat.

56. A multi-component composite according to claim 55, wherein the 5 composition is transparent when cured.

57. A method for making a multi-component composite comprising:

(a) applying a pigmented coating composition to a substrate to form a basecoat;

10 (b) applying a coating composition according to claim 1 as a topcoating composition over at least a portion of the basecoat; and

(c) curing the coating composition to form a cured coating.

58. A method according to claim 57, wherein the topcoating composition 15 is cured by exposure to (1) ionizing radiation or actinic radiation and (2) thermal energy after application to the substrate.

59. A method for improving the scratch resistance of a polymeric substrate or polymer coated substrate comprising forming a composition 20 according to claim 1 over at least a portion of the substrate.

60. A method for retaining the gloss of a polymeric substrate or polymer coated substrate over a predetermined period of time comprising forming a composition according to claim 1 over the surface of the substrate.

25

61. A method for revitalizing the gloss of a polymeric substrate or polymer coated substrate comprising forming a composition according to claim 1 over the surface of the substrate.

30 62. A coating composition formed from components comprising:

- (a) a first material comprising at least one radiation curable reactive functional group;
 - (b) a second material comprising at least one thermally curable reactive functional group;
- 5 (c) at least one curing agent reactive with the at least one thermally curable reactive functional group, the at least one curing agent being selected from aminoplast resins, polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing; and
- 10 (d) a plurality of particles,
 wherein each component is different.

63. A composition according to claim 62, wherein the composition when cured has an initial scratch resistance value such that after scratch testing
15 greater than 40 percent of the initial 20° gloss is retained.

64. A composition according to claim 62, wherein the composition when cured has a retained scratch resistance value such that after scratch testing greater than 30 percent of the initial 20° gloss is retained.

20

65. A cured coating formed from the composition of claim 62.

66. A coated substrate comprising a substrate and a composition according to claim 62 deposited over at least a portion of the substrate.

25

67. A method for forming a cured coating on a substrate comprising applying over at least a portion of the substrate a coating composition according to claim 62.

68. A method according to claim 67, wherein the coating composition is cured by exposing the coating composition to (1) actinic or ionizing radiation and (2) thermal energy after application to the substrate.

5 69. A method according to claim 67, wherein the substrate is an automotive substrate.

10 70. A coated automobile substrate comprising an automobile substrate and a composition according to claim 62 deposited over at least a portion of the automobile substrate.

15 71. A multi-component composite coating composition comprising a basecoat deposited from a pigmented coating composition, and a composition according to claim 62 applied over at least a portion of the basecoat.

72. A method for making a multi-component composite comprising:
(a) applying a pigmented composition to a substrate to form a basecoat;
(b) applying a coating composition according to claim 62 as a topcoating composition over at least a portion of the basecoat; and
20 (c) curing the coating composition to form a cured coating.

25 73. A method for improving the scratch resistance of a polymeric substrate or polymer coated substrate comprising forming a composition according to claim 62 over at least a portion of the substrate.

74. A method for retaining the gloss of a polymeric substrate or polymer coated substrate over a predetermined period of time comprising forming a composition according to claim 62 over the surface of the substrate.

75. A method for revitalizing the gloss of a polymeric substrate or polymer coated substrate comprising forming a composition according to claim 62 over the surface of the substrate.

5 76. A coating composition formed from components comprising:

(a) at least one material comprising at least one ultraviolet radiation curable reactive functional group and at least one thermally curable reactive functional group;

10 (b) at least one curing agent reactive with the at least one thermally curable reactive functional group, the at least one curing agent being selected from polyisocyanates, blocked polyisocyanates, triazine derived isocyanates, polyepoxides, polyacids, polyols and mixtures of the foregoing; and

(c) a plurality of particles,
wherein each component is different.

15

77. A composition according to claim 76, wherein the composition when cured has an initial scratch resistance value such that after scratch testing greater than 40 percent of the initial 20° gloss is retained.

20

78. A composition according to claim 76, wherein the composition when cured has a retained scratch resistance value such that after scratch testing greater than 30 percent of the initial 20° gloss is retained.

25

79. A cured coating formed from the composition of claim 76.

80. A coated substrate comprising a substrate and a composition according to claim 76 deposited over at least a portion of the substrate.

30 81. A method for forming a cured composition on a substrate comprising applying over at least a portion of the substrate a coating composition according to claim 76 and curing the coating composition after application to the substrate.

82. A coated automobile substrate comprising an automobile substrate and a composition according to claim 76 deposited over at least a portion of the automobile substrate.

5

83. A multi-component composite coating composition comprising a basecoat deposited from a pigmented coating composition, and a composition according to claim 76 applied over at least a portion of the basecoat.

10

84. A method for making a multi-component composite comprising:

- (a) applying a pigmented composition to a substrate to form a basecoat;
- (b) applying a coating composition according to claim 76 as a topcoating composition over at least a portion of the basecoat; and
- (c) curing the coating composition to form a cured coating.

15

85. A method for improving the scratch resistance of a polymeric substrate or polymer coated substrate comprising forming a composition according to claim 76 over at least a portion of the substrate.

20

86. A method for retaining the gloss of a polymeric substrate or polymer coated substrate over a predetermined period of time comprising forming a composition according to claim 76 over the surface of the substrate.

25

87. A method for revitalizing the gloss of a polymeric substrate or polymer coated substrate comprising forming a composition according to claim 76 over the surface of the substrate.

INTERNATIONAL SEARCH REPORT

Inte	Application No
PCT/US 00/20839	

A. CLASSIFICATION OF SUBJECT MATTER					
IPC 7	C09D4/06	C09D4/00	C09D133/04	C09D175/14	C08G18/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 212 901 A (VAN NEERBOS ABRAHAM ET AL) 15 July 1980 (1980-07-15) column 4, line 11 - line 37 examples claim 7 ---	1-87
X	WO 98 40170 A (MAAG KARIN ;DOESSEL KARL FRIEDRICH (DE); HERBERTS & CO GMBH (DE)) 17 September 1998 (1998-09-17) page 6, line 5 - line 13 examples ---	1-87
X	EP 0 928 800 A (BAYER AG) 14 July 1999 (1999-07-14) claims --- -/-	1-87

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

16 October 2000

Date of mailing of the international search report

23/10/2000

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Pollio, M

INTERNATIONAL SEARCH REPORT

Inte Application No
PCT/US 00/20839

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 00456 A (CIBA SC HOLDING AG ;VALET ANDREAS (DE)) 8 January 1998 (1998-01-08) page 21, line 15 - line 29 examples 5-8 claim 1 -----	1-87
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